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# TRANSLATION

UTILIZATION OF DIESEL OILS WITH ADDITIVES

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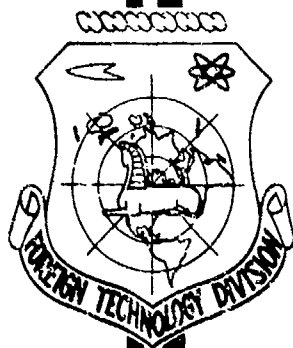
G. A. Morozov

## FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE

OHIO



## EDITED TRANSLATION

UTILIZATION OF DIESEL OILS WITH ADDITIVES

BY: G. A. Morozov

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(This book gives the properties of diesel oils with additives, and laboratory- and operating-test results for diesels of various types. It has been compiled on the basis of a generalization of advanced experience gained in the development, testing, and application of new types of diesel oils and additives.

The book is designed for engineers and technicians working in petroleum refineries or diesel-engine manufacturing plants or in organizations concerned with the applications of diesel oils, and may also prove useful to students in the technical higher educational institutions.)

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## INTRODUCTION

The growing number of engines of all types, and in particular the increased production of diesel locomotives, tractors, and marine and stationary diesel engines require fuels and lubricating oils of ever higher quality.

To meet the requirements of the national economy of the Soviet Union for petroleum products, the seven-year plan provides for a petroleum-production goal of up to 230-240 million tons per year in 1965. Over this period, the production of lubricating oils should be doubled. The problem of motor lubricating-oil quality and variety has become especially important.

Advances in diesel-engine design, increased diesel combustion intensity, the need for the broad-scale utilization of sulfur-bearing fuels with a simultaneous increase in engine reliability and service life - all these factors make it necessary to improve lubricating-oil quality considerably.

Modern oils, designed to lubricate supercharged diesel engines should be considered to be mixtures consisting of an oil base (the base oil) and additives designed to improve those operating characteristics that cannot be bettered with the aid of ordinary petroleum-refining and oil-purification methods. Thus, a radical improvement in diesel-oil quality may be obtained primarily by choosing sufficiently effective additives. Here we are concerned to increase precisely those oil quality indicators that do not satisfy the operating requirements of actual engine types.

A similar situation exists with respect to two requirements for fuels and oils for other types of engines as well.

This fact has opened up a new field of technology - the application of petroleum products.

The problems of choosing, using, and increasing the quality of oils and additives for various types of engines may be solved only by the combined efforts of petroleum chemists, machine designers, and operating personnel. K.K. Papok mentioned a situation specifically, saying that "at the junction of two completely different branches of science and technology, the chemistry and technology of petroleum on the one hand, and machine design on the other, the past 30-35 years has seen a new branch of science and technology arise - the application of fuel and oil in motors and machinery."\*

In the present work, the author has attempted to generalize experience gained over recent years in the utilization of oils with additives in diesel engines, in order to help solve the problem of increasing diesel-oil quality.

## Chapter 1

### PRESENT-DAY VARIETY AND QUALITY OF DIESEL OILS

#### PROSPECTS FOR DEVELOPMENT OF DIESEL-ENGINE DESIGNS AND BASIC REQUIREMENTS FOR DIESEL-OIL QUALITY

The 1959-1965 plan for the development of the national economy of the Soviet Union provides for a considerable increase in the production of diesel locomotives, ships, a high level of agricultural mechanization, an increase in construction and road-building activities, and the growth of other branches of industry and transportation; all of this requires a major increase in the production of chips of various powers, types, and functions.

The basic tasks facing the domestic diesel-engine industry over this period involve increasing the efficiency, reliability, and lifetime of the diesel engines manufactured.

A characteristic feature of diesel-engine development may be considered to be the widespread utilization of gas-turbine supercharging and the perfection of the operating cycle with the aim of improving the efficiency with which the cylinder working volume is utilized, raising fuel economy, and decreasing the weight-horsepower ratio of the engines.

The possible further development of diesel supercharging by the use of gas turbines may have as a consequence some increase in engine combustion intensity; the requirements for lubricating-oil quality will therefore be more severe.

Another feature of diesel-engine development is the need for

widespread utilization of sulfur-bearing diesel fuels; where oil quality is inadequate, this may lead to a decrease in the motor potential.

Thus, the solution of the problems raised by these trends in diesel development requires a considerable increase in the quality of the lubricating oils used.

Combustion intensity in diesels. The temperatures of the surfaces in the engine cylinder-piston system, with which the oil is in constant contact, are of decisive importance for the rate of oil oxidation and subsequent thermal decomposition, i.e., for the processes of carbon formation, corrosion, and wear. The higher the temperature of the piston in the region of the side surface and the ring grooves, the more vigorous the thermal decomposition of the oil with formation of carbon and varnish; this results in a loss of piston-ring mobility, and impairment of piston thermal conductivity.

TABLE 1. Piston Temperatures for Several Types of Diesel Engines

1		2 Температура, °C	
Тип двигателя		3 длина поршня (максимальная)	4 поршня в районе верхний кольцевой канавки
5	48,5/11	235	150—160
6	410,5/13	235	212
7	423/30	225—260	220
	41118/20	350	240—250
	2Д-100	320	256

1) Type of engine; 2) temperature, °C; 3) piston crown (maximum); 4) piston in region of top ring groove; 5) Ch; 6) ChN; 7) D.

Engine combustion intensity depends on a full series of structural factors and the peculiarities of the working cycle (excess air coefficient, cooling setup, etc.), but in general, the combustion intensity increases as the mean effective pressure goes up.

Figure 1 shows a standard piston temperature distribution.

Table 1 gives results of piston-temperature measurements for several types of diesel engines.

As the data show for the types of engines indicated, the maximum piston-crown temperature fluctuates over quite a broad range, but in the region of the top piston ring, the temperature does not exceed  $250^{\circ}\text{C}$ . As a rule, the utilization of gas-turbine supercharging elevates piston temperature somewhat.

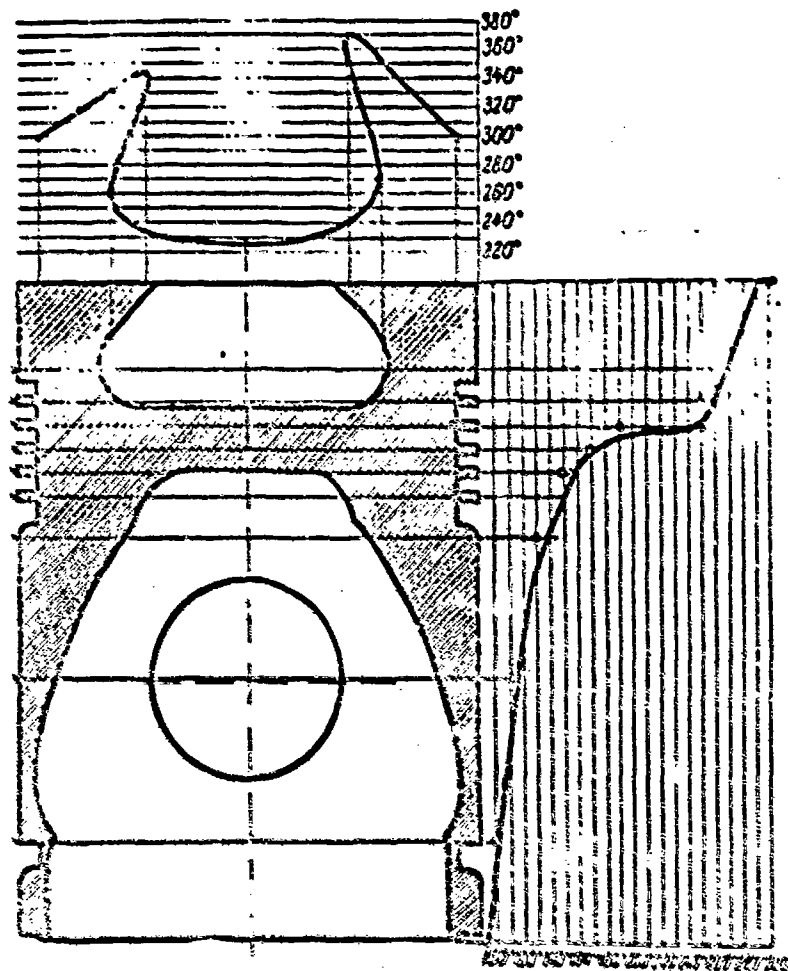


Fig. 1. Temperature distribution for piston of Ch23/30 diesel engine (with chamber in piston).

Thus, for example, with 0.5 atm supercharging of a Ch10.5/13 engine, the maximum piston-crown temperature rises from 225 to  $235-237^{\circ}\text{C}$ , while the temperature in the region of the top piston ring increases from 212 to  $230^{\circ}\text{C}$ .

Figure 2 shows the variation in piston temperature for a 6Ch23/30 engine (data of the Central Diesel Scientific Research Institute) supercharged from 600 to 900 horsepower by means of gas-turbine supercharging.

Engine combustion intensities may be characterized directly through data obtained by measuring the temperature of the piston side wall, in particular the temperatures in the area of the top piston compression rings, where the carbon- and varnish-formation processes are most intense. There is almost no detailed system having data presently available for all types of diesel engines, and the sparse temperature-measurement results available cannot be compared reliably, owing to the differences in the methods of determination used. It is therefore necessary to characterize the combustion intensities with the aid of parameters that determine the degree of engine supercharging.

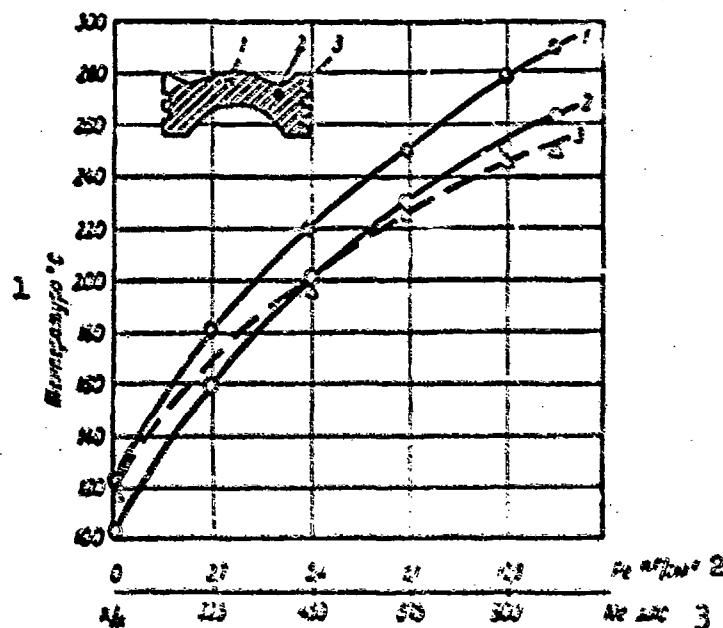


Fig. 2. Temperature variation for piston Ch23/30 diesel with power output increased by supercharging (the numbers 1, 2, and 3 indicate points at which piston temperature was measured). 1) Temperature, °C; 2) kg/cm<sup>2</sup>; 3) effective horsepower.

The combustion intensity of an engine depends primarily on the

TABLE 2. Classification of Diesel Engines on Basis of Supercharging

1  Группа		2 Тип двигателей и основные параметры							
		3  Тип	4  Марка	5  Мощность двига- теля, э. л. с.	6  Число оборотов, об/мин	7  Средняя скорость поршня, м/сек	8  Среднее эффек- тивное давление, кг/см²	9  Критерий форси- ровки K <sub>Ф</sub>	
10	Высоконапряжен- ные дизели (K <sub>Ф</sub> больше 50)	Специальные двига- тели 11	—	—	9—12	8—20	50— 100		
	12	Дизели средней напряженности (K <sub>Ф</sub> от 30 до 50)	14 12ЧН18/20 Д108/12,7 10Д20,7 2х25,4	16 ЯАЗ 206 15 Д100	900 165 2000	1650 2000	11,0 8,5	7,8 5,3	46,2 45,1
14 12ЧН18/20		М-751	750	1500	10,0	7,7	38,5		
14 12ЧН18/20		М-601	700	1400	9,35	6,7	31,5		
14 6ЧН31,8/33		Д-50	1000	740	8,15	7,7	31,4		
15		—	—	—	—	—	—		
13	Малонапряжен- ные дизели (K <sub>Ф</sub> менее 30)	8Д43/61	15	—	2000	250	5,1	5,1	26,0
		6Д30/50	5	—	600	300	5,0	4,25	21,2
		6Ч15/18	11	18Д6	150	1500	9,0	4,7	21,2
		17 4Ч14,5/20,5	19	КДМ-46	93	1000	6,8	6,15	20,5
		17 4Ч10,5/13	19	—	40	1500	6,5	5,3	17,7
		17 6Ч12/14	19	Б-150	80	1500	7,0	5,0	17,6
		17 4Ч12,5/12,5	15	Д-14	14	1600	6,7	5,1	17,3
		17 4Ч12,5/15,2	15	Д-54	54	1300	6,7	5,0	16,8
		17 4Ч10,5/13	15	Д-35	37	1400	6,0	5,8	16,1
		17 6Ч36/45	—	—	600	375	5,6	5,2	14,7
		17 4Ч18,5/11	—	—	20	1500	5,5	4,8	13,2

1) Group; 2) engine type and basic characteristics; 3) type; 4) designations; 5) engine power, effective horsepower; 6) speed, rpm; 7) mean piston speed, m/sec; 8) mean effective pressure, kgf/cm<sup>2</sup>; 9) supercharging criterion K<sub>Ф</sub>; 10) high-intensity diesels (K<sub>Ф</sub> greater than 50); 11) special engines; 12) medium-intensity diesels (K<sub>Ф</sub> from 30 to 50); 13) low-intensity diesels (K<sub>Ф</sub> below 30); 14) ChN; 15) D; 16) YaAZ; 17) Ch; 18) ZD; 19) KDM.

mean effective pressure  $p_e$ .

In comparing the combustion intensities of different types of diesels, it is convenient to use the supercharging criterion K<sub>Ф</sub>, which characterizes the efficiency with which the working volume of the cylinder is used;

$$K_{\Phi} = p_e \cdot C_m \cdot z,$$

where  $p_e$  is the mean effective pressure, kg/cm<sup>2</sup>;  $C_m$  is the mean piston



speed, m/sec;  $z$  is a cycle factor ( $z = 0.5$  for four-cycle engines,  $z = 1.0$  for two-cycle engines).

There is no basis for expecting an increase in  $K_f$  due to any considerable increase in  $C_m$ , since this will be limited by the strength of the material.

On the other hand, the possibilities for increasing  $p_e$  are good where gas-turbine supercharging is used. The future development of diesel-engine design will see an increase in the mean effective pressure from  $p_e = 5-6 \text{ kg/cm}^2$  to values of:

for 4-cycle diesels,  $p_e = 20-25 \text{ kg/cm}^2$ ;

for 2-cycle diesels,  $p_e = 12-14 \text{ kg/cm}^2$ .

Domestically-produced diesels may be classified on the basis of supercharging into three basic groups (Table 2).

The first group includes the most highly supercharged engines, using gas turbines, which have values of  $K_f$  exceeding 50, mean piston speeds  $C_m$  above 9 m/sec, and piston temperatures in the region of the top piston ring that normally exceed  $250^\circ\text{C}$ . Here we have included certain special-purpose engines and individual preproduction diesel models that use a high degree of supercharging and that are presently undergoing tests or are in the final stages of development.

To characterize the diesels in this group, we have given the characteristics of several present-day highly supercharged engines produced by foreign companies:

	$N_e$	$n$	$C_m$	$p_e$	$K_f$
MAN (6ChN30/50) .....	1700	400	6.0	20	60
Cummins (CNS10.5/12.7) .....	300	3600	15.2	11.4	87
Sulzer (6D18/22.5x2) .....	2750	1000	7.5	12.5	94

The second group includes several series of supercharged locomotive and marine diesels (Types M-50, 2D100, D-50, etc.), with super-

TABLE 3. Petroleum-Production Increase in Urals-Volga District, %

1 Год	2 Всего по СССР	3 В том числе		
		Урало-Волж- ский район 4	Южные районы 5	Прочие районы 6
1940	100	6,0	86,4	7,6
1956	100	62,9	27,0	10,1
7 1965 (план)	100	80	20	

1) Year; 2) entire USSR; 3) including; 4) Urals-Volga District; 5) Southern District; 6) other districts; 7) planned.

TABLE 4. Proportions of Low-Sulfur and High-Sulfur Diesel Fuels to be Produced over 1959-1965 Period, %

	1959 г.	1965 г.
1) Малосернистое дизельное топливо (содержание серы от 0,2 до 0,6%) . . . . .	23,2	59,0
2) Сернистое дизельное топливо (содержание серы от 0,6 до 1,0%) . . . . .	65,7	31,1

1) Low-sulfur diesel fuel (sulfur content, 0.2 to 0.6%); 2) high-sulfur diesel fuel (sulfur content, 0.6 to 1.0%).

charging indices  $K_f$  ranging from 30 to 50 and piston temperatures in the region of the top compression ring of the order of 250°C.

The third group includes relatively low-intensity diesels with values of  $K_f$  below 30. The corresponding piston temperature is normally below 250°C; thus, for example, for the Ch10.5/13 diesel, it lies in the 210-220°C range.

Utilization of sulfur-bearing fuel. In order to satisfy the requirements of the national economy for petroleum products, and primarily for fuels and oils, the output of petroleum will rise to 230-240 million tons by 1965. The production of diesel fuels and oils may be increased chiefly by increasing the extraction and refining of sulfur-bearing crudes from Eastern fields.

While before the war the requirements for diesel fuels and oils

were met basically by refining low-sulfur Baku, Grosnyy, and other Southern crudes; at the present time a considerable number of the diesel engines produced in increasing numbers during the postwar five-year plans use fuel obtained from Vtoroy Baku crudes, i.e., from Ural-Volga fields; as is well known, high sulfur content is characteristic of these crudes.

The considerable increase in the relative importance of Ural-Volga crudes with respect to the total production of the petroleum industry of the Soviet Union may be seen clearly from the data [46] given in Table 3.

It follows from this data that by 1965 as much as 80% of all petroleum will be extracted in the form of sulfur-bearing and high-sulfur crudes. Thus, petroleum refiners can expect a reduction in the quality of the crude stock.

Although before the war the sulfur content of diesel fuel did not exceed 0.2% on the average, at the present time, the majority of diesel engines at work in the national economy, including tractor, locomotive, marine, and stationary engines, use GOST 305-58 diesel fuel which contains up to 1.0% sulfur.

The proposed relationship between diesel fuels of various sulfur contents and total production for the 1959-1965 period is shown in Table 4.

We remove sulfur from fuels by the hydrogenation (hydrogen refining) method on a limited scale. The future plans for the petroleum-refining industry provide for the introduction of additional capacity for hydrogen refining of petroleum products, and in the future, the production of purified (low-sulfur) fuel will rise, and the relative consumption of high-sulfur fuels (0.5 to 1.0% sulfur) will gradually decrease, as we can see from the data given in Table 4.

Nonetheless, for the near future, the consumer must reckon with the need for broad-scale utilization of high-sulfur fuels and oils.

As we know, utilization of high-sulfur fuels results in increased wear and carbon formation. The replacement of Baku oils with oils made from Eastern sulfur-bearing crudes will also increase the amount of varnish and carbon deposited on the engine. Thus, high-sulfur fuels can be used in diesel engines and the necessary motor potential retained only if oils with sufficiently effective additives are used.

The increase in engine motor potential, i.e., the increased engine service life before major repair is required, demands primarily a decrease in the wear of the basic moving pairs under service conditions.

It is an especially difficult task to increase motor potential in view of the need for the broad-scale utilization of high-sulfur fuels, since combustion products of high-sulfur fuels increase wear and carbon formation, and accelerate the aging process in lubricating oils.

The problem of extending engine life must be solved by improving the quality of parts manufacture, selecting wear-resistant materials, making use of heat treatment, protective coatings, and fuel additives as well as by improving the quality of the lubricants used.

TABLE 5. Oil Burnt by GAZ-51 Engines in Various Conditions

1 Состояние двигателя	2 Среднее ур-е масла		
	3 г./час	4 % к норме по ГОСТу	5 % к расходу топлива
6 Новый	238.0	408	3.11
7 Новый после смены поршней и колец	171.0	272	2.07
8 Старый	63.1	100	0.76

1) Engine condition; 2) average amount of oil burnt; 3) g/hr; 4) % of

new-engine loss; 5) % of fuel consumption; 6) worn; 7) worn, following replacement of pistons and rings; 8) new.

Decreasing oil consumption. Another important task facing diesel-engine manufacturers and petroleum refiners is that of decreasing the amount of oil consumed by diesels.

At the present time, the average oil consumption in diesel engines is 4.5-5.0% of the fuel consumption, and it exceeds the average oil consumption in the United States.

Engine oil consumption consists of: a) burnt oil; b) the fresh oil used to replace spent oil. The amount of oil burnt by an engine is relatively independent of the grade of oil, since any petroleum oil entering the upper zone of the cylinder barrel and coming into contact with the hot gases - the fuel combustion products - will undergo vigorous thermal decomposition, i.e., it will burn up. The amount of oil burnt depends primarily on the condition of the engine.

Table 5 shows data due to N.V. Brusyantsev [5] on the oil burnt by GAZ-51 engines depending on condition.

Future plans for diesel-engine design development call for a decrease in average oil consumption to 3.0% of the weight of fuel consumed for marine, stationary, and mobile diesel engines and a reduction to 2.5% for automotive diesels.

Oil consumption may be reduced by: 1) improving oil quality; 2) extending the useful life of the oil in the engine by increasing its stability and improving purification devices (filters, centrifuges); 3) by regeneration of spent oil.

By raising oil quality (improving viscosity-temperature characteristics, detergency, and thermal stability) it will be possible to decrease the amount of oil burnt and extend the useful life of the oil in an engine.

Thus, looking at all of these trends in diesel development for the next few years, e.g., increasing combustion intensity, greater motor potential, utilization of high-sulfur fuels, and decreased oil consumption, we must conclude that a considerable improvement in the quality of domestic lubricating oils is needed. As we have already noted, it is possible to raise oil quality both by improving the basic oil and by choosing appropriate additives. The high quality of the best modern oils is achieved basically by introducing into the composition of the oil additives that make it possible to obtain performance characteristics satisfying the needs of engine operation. In recent years, therefore, a great deal of attention has been devoted to problems in the development, choice, and testing of additives, the investigation of the mechanisms by which they act, and the development of additive technical specifications applicable to actual engine types.

#### MOST IMPORTANT PHYSICOCHEMICAL PROPERTIES OF DIESEL OILS AND THEIR EFFECT ON ENGINE OPERATION

The basic function of a lubricant consists in decreasing friction losses and reducing wear on the working surfaces of engine or mechanism components.

In addition, an oil performs several other functions such as protecting the engine against corrosion, and cooling the working surfaces. The tendency of an oil to deposit carbon and varnish on hot engine parts should be reduced to a minimum, it should possess adequate thermal-oxidation stability, and it should retain its composition and properties for an extended period of time under service conditions.

For an oil to be suited to its functions, it should satisfy specific technical specifications. The development and formulation of such oil specifications for specific engine types involves some difficulty owing to the fact that the methods known to us for evaluating

oil quality are still imperfect, and a definitive judgment as to the suitability of a given type of oil can be made, as a rule, only after extended bench or operating tests.

As we have already noted, the properties of present-day oils represent the properties of the base oil as affected by additives, which improve certain performance characteristics. Thus, in the present section we shall be concerned primarily with the fundamental properties of the base oil, and we shall not be concerned with the effects of various additives. This question is discussed in subsequent sections.

As with any petroleum product, lubricating oils represent a mixture of many hydrocarbons of various structures. From the viewpoint of physical chemistry, the properties of an oil are determined solely by the composition and structure of its component hydrocarbons.

In turn, the chemical compositions of oils depend both on the nature of the crude and on the petroleum-refining and oil-purification techniques used. Thus, in order to compile actual technical specifications for oil quality applicable to oils of various functions, it is necessary to be conversant with the basic concepts of production methods, the important physicochemical properties, and the importance of these properties under operating conditions.

Production of lubricating oils. Lubricating oils are obtained during distillation of petroleum by removing the appropriate distillation products and then refining them. In accordance with the method used to produce them, oils are classified as distillates, residuals, and blended oils. The majority of low-viscosity oils, such as motor oils, machine oils, etc. are distillates. Residual oils are the high-viscosity residues from distillation of low-gum petroleum; they go through special refining processes. Many oils are also obtained by blending distillate and residual oils.

Lubricating oils are produced in atmospheric-reduced pressure installations (AVT) in which the heavy oil remaining after the gasoline and kerosene-gas oil fractions have been driven off from the petroleum are again distilled in the vacuum section of the installation, with the oil fractions being removed; the residue obtained (semiasphalt) is used in the production of residual oils.

On the basis of refining method, oils may be classified arbitrarily as acid-mechanically refined or solvent-refined oils.

During sulfuric-acid processing, undesirable resinous compounds and asphaltenes are removed from the oils.

After sulfuric-acid purification, oils are treated with alkali and subjected to mechanical purification with fuller's earth.

Oils obtained from tarry crudes require large quantities of sulfuric acid in refining, and yield small amounts of finished product; this is economically undesirable, and thus another refining method is used for such oils, called deasphaltization. Deasphaltization consists in treating the oil with liquid propane. The oil is dissolved in the propane, and the asphaltenes and most of the tars separate out into the residues.

The action of selective solvents is based on their ability to dissolve some specific components of the oil. Phenol, furfurool, nitrobenzene, etc. are selective solvents of this type.

The part of the oil purified by the selective solvent is called raffinate; it consists basically of alkane, cyclane, and certain aromatic hydrocarbons. The extracted portion of the oil, i.e., the part removed by the solvent, contains polycyclic hydrocarbons as well as naphthenic acids, tars, asphaltenes, and other compounds containing acids.

Oils containing large quantities of paraffins have high pour



points, and should be put through a deparaffinization process; this consists in adding solvents, cooling the oil solution to a sufficiently low temperature, and removing the crystallized paraffin.

The yields and boiling ranges of the fractions depend on the nature of the petroleum being processed and on the purposes for which the final oils are to be used. The boiling ranges of such oils as motor-10, diesel D-11 normally lie in the 300-330 to 520-530°C range, adjusted for atmospheric pressure.

When light Bibi-Eybatskiy petroleum is distilled, the yield of residual oil is about 50% of the crude, while the yield of all oily fractions is 63-65% of the residual oil entering the vacuum section of the installation.

Viscosity or internal liquid friction is a very important oil property, which is responsible for the creation of a strong oil film on rubbing surfaces and for the sealing of gaps.

The unit of dynamic viscosity is the poise (pz), which represents the internal friction that appears when two liquids 1 cm<sup>2</sup> in area move with respect to each other for a distance of 1 cm at a speed of 1 m/sec under a force of 1 dyne.

The dimensions of the poise are dyne.sec/cm<sup>2</sup>, or g/cm/sec.

The kinematic viscosity is the ratio of the dynamic viscosity to the density of the liquid. The unit of kinematic viscosity is the stoke (st), whose dimensions are cm<sup>2</sup>/sec. One one-hundredth of a stoke is a centistoke (cst).

The relative viscosity is the viscosity expressed in relative units, and it is obtained from various viscosimeters. In the USSR, relative viscosity is expressed in degrees VU, which correspond to degrees Engler.

Practical experience has shown that to provide reliable lubrica-

tion of most medium-intensity diesel engines with piston speeds of up to 7-8 m/sec, it is necessary to use oils with kinematic viscosities in the 10-12 sst range at 100°C. For higher-intensity diesels with piston speeds of 8-10 m/sec, oils with viscosities of 14-20 sst at 100°C are used.

It should be noted that there is no point in attempting to use oils with too-high a viscosity.

As we know from the hydrodynamical theory of lubrication, developed by N.P. Petrov, the friction factor ( $f$ ) is defined by the expression

$$f = \eta \frac{V}{hP}$$

where  $\eta$  is the dynamic viscosity of the oil in kg·sec/m<sup>2</sup>;  $V$  is the speed at which the rubbing surfaces move, m/sec;  $h$  is the thickness of the oil layer separating the rubbing surfaces, m;  $P$  is the relative load, kg/cm<sup>2</sup>.

TABLE 6. Limiting Viscosities Providing Oil Pumpability and Engine Starting (Data Due to N.G. Puchkov)

1 Двигатель	2 Вязкость масла (сст), обеспечивающая	
	3 прокачиваемость	4 запуск
5 ГАЗ-51	25 000—30 000	18 000—20 000
6 ЗИЛ-120:		
7 стартер СТ-45	11 000	3000—4000
7 стартер СТ-45	30 000	11 000

1) Engine; 2) oil viscosity (sst) guaranteeing; 3) pumpability; 4) starting; 5) GAZ-51; 6) ZIL-120; 7) ST-45 starter.

The formula given holds for the case of fluid friction. It follows from the formula that the energy expended on overcoming friction will be directly proportional to the viscosity of the oil. According to the data of NATI [Scientific Research Institute for Automobiles and

Tractors], if MK-22 oil replaces D-11 oil in a D-35 engine, a power loss of 6% will result.

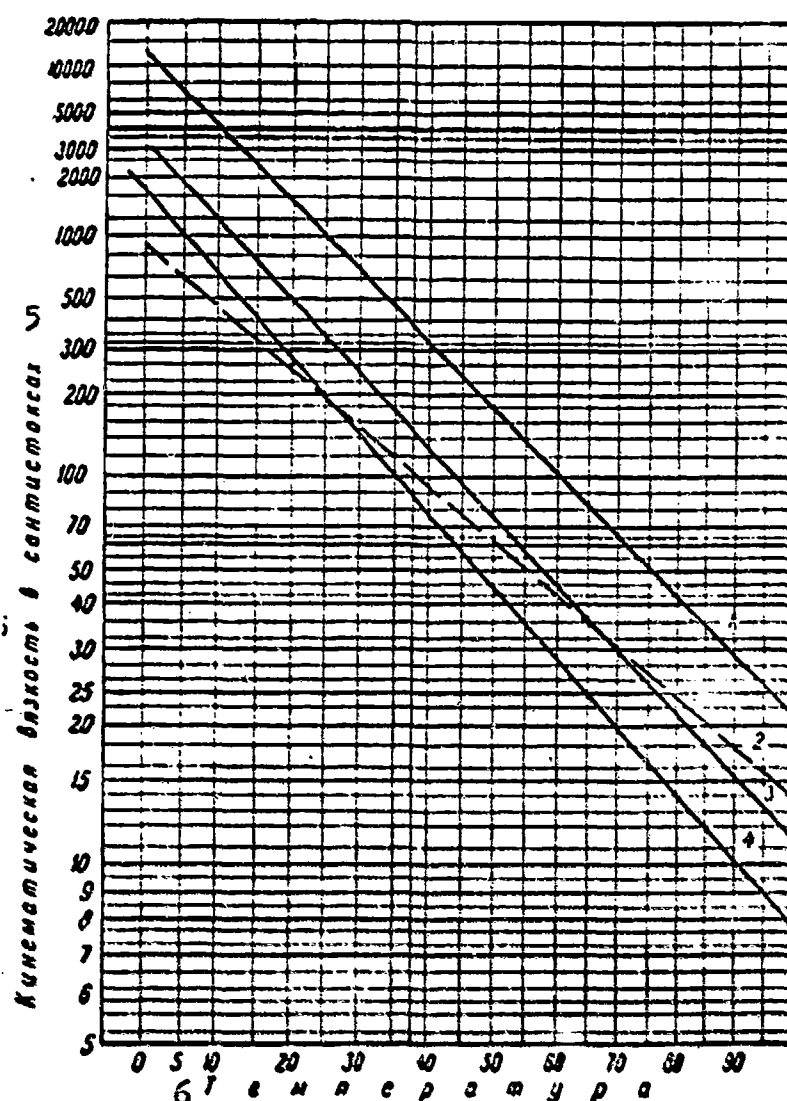


Fig. 3. Oil viscosity-temperature curves. 1) MK-22; 2) MT-14p; 3) Dp-11; 4) Dp-8; 5) kinematic viscosity, centistokes; 6) temperature.

In addition, high oil viscosity hampers engine starting. High-viscosity oils are recommended not only for the engines mentioned, which have high piston speed, but also for diesels operated in Southern areas, under elevated ambient temperatures, and for lubricating heavily worn engines. On the other hand, winter diesel oils should be lower in viscosity (Dp-8 oil).

The oils used for carburetor-type automobile and tractor engines

are less viscous than those used for diesels, and requirements for such oils may be satisfied by the range of automobile oils (motor oils) having viscosities of from 5-6 to 14-15 sst at 100°C.

The concept of the limiting viscosity for which oil pumpability in the engine system and engine starting are guaranteed is used to evaluate the starting properties of oils. Limiting-viscosity values may fluctuate within quite a broad range, depending on the type of engine, the starter, and other elements of the starter system.

M.P. Volarovich believes that for easy starting of automobile engines, oil viscosity at the starting temperature should be no more than 9000-10,000 sst.

Table 6 gives data on oil limiting viscosity for various types of automotive engines [36].

Figure 3 shows the way in which viscosity depends on temperature for several oils used in diesel engines.

Oiliness or the lubricating ability of an oil is a concept that is introduced in order to characterize the strength of the oil film under boundary-lubrication conditions.

While under fluid-lubrication conditions, the strength of the oil film is determined primarily by the viscosity of the oil, under boundary-friction conditions, the strength of the oil film is affected substantially by the presence in the oil of surface-active (polar) molecules, which provide the strong contact between the oil film and the metal surface.

The surface-active materials include naphthene and fatty acids, asphalt-resin substances, and sulfur compounds [50]. Vegetable oils (such as castor oil) are considerably better with respect to oiliness than petroleum oils. Heavy refining of oils removes the asphalt-resin compounds, thus impairing the lubricating ability.

Vegetable oils and mixtures of vegetable oils with mineral oils, however, have poor oxidation stability, and thus they have not found wide application as engine lubricants.

High oil-film strength is necessary primarily to ensure reliable lubrication of parts subject to high pressures such as the various types of gear drives (transmission oils). Here the lubricating ability of an oil may be increased by the utilization of additives, which are called antiwear or antiscoring additives. Such additives include high-molecular-weight organic acids and their salts, sulfured oils, and various compounds containing sulfur or phosphorus.

Oiliness is normally evaluated by means of tests on some given friction machine. The most common evaluation method employs a four-ball friction machine of well-known design for the tests. It should be noted, however, that oil-evaluation results obtained by means of friction machines do not always agree with results obtained under actual service conditions [5].

Oil oxidizability. During engine operation, the lubricating oil is subjected to a process of oxidation, primarily under the influence of the oxygen in the air and high temperatures. The accumulation in an oil of such oxidation parts as hydroxy acids, gums, and asphaltenes is the basic factor responsible for the appearance of various engine deposits - carbon, varnish, and residues (sludge) in the oil. The formation of peroxides and acids is responsible for oil corrosiveness. A considerable accumulation of oxidation products in the oil may necessitate the complete elimination of the oil from the engine lubrication system and substitution of fresh oil.

The ability of an oil to resist oxygen reaction is called the oxidation stability, or the thermal oxidation stability. Oil oxidation stability is a very important property and thus the study of condi-

tions affecting the oxidation process has been the subject of many investigations.

Hydrocarbons oxidize in stages, passing through various intermediate steps, and oxidation depends on the structure of the hydrocarbons and the conditions under which the process occurs.

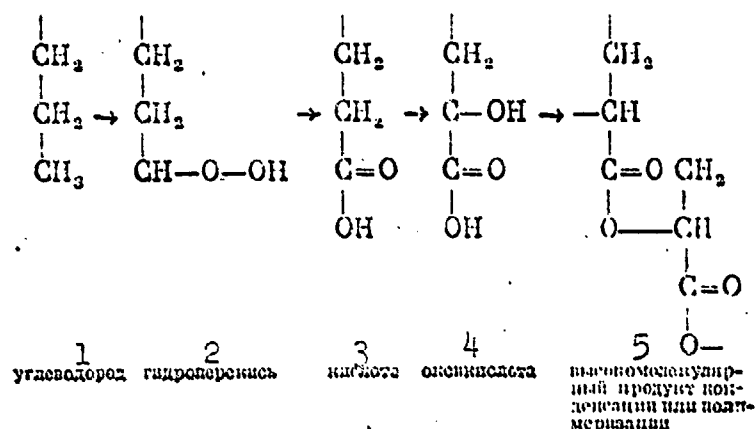
The most readily oxidized hydrocarbons are the paraffins, followed by the naphthenes, while the aromatic hydrocarbons prove to have the greatest oxidation stability. Thus, the alkylated aromatic hydrocarbons, which also have the flattest viscosity curve, are a very valuable component of an oil. Hydrocarbons of hybrid structure such as naphthene-aromatic or alkylated aromatic hydrocarbons, which have long side paraffin chains, also prove to be readily oxidizable.

Hydrocarbon-mixture oxidation differs in nature from pure-hydrocarbon oxidation, since the individual hydrocarbon groups mutually affect the acceleration or retardation of oxidation reactions. Thus, compounds of the phenol type are strong antioxidants.

Thus, for oils that are mixtures of many hundreds of hydrocarbons of differing structure, the oxidation process is extremely complicated.

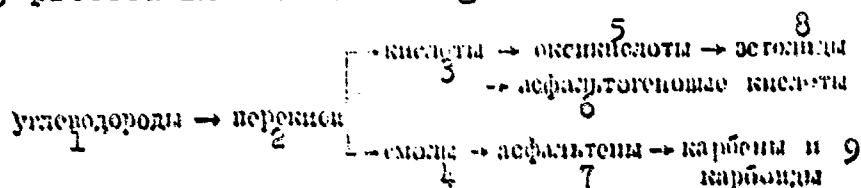
Oil oxidation has been studied in great detail by N.I. Chernozhukov and S.E. Kreyn, as well as by K.A. Ivanov and other researchers. It has been established that the first intermediate oxidation products for hydrocarbons are peroxides. Peroxides are unstable compounds that later are transformed into acids and hydroxy acids. In addition, aldehydes, ketones, and alcohols may be obtained as intermediate oxidation products. Further oxidation of these products leads to thickening and the formation of condensation and polymerization products known as asphaltenes, estolides, gums, etc., which are precisely the substances that form varnish, carbon, and sludge in the oil.

A somewhat simplified oxidation scheme for oil hydrocarbons (omitting several intermediate oxidation compounds such as aldehydes, alcohols, etc.) may be given in the following form:



1) Hydrocarbon; 2) hydroperoxide; 3) acid; 4) hydroxy acid; 5) high-molecular-weight condensation or polymerization product.

According to N.I. Chernozhukov and S.E. Kreyn [50], hydrocarbon oxidation may proceed in the following two directions:



1) Hydrocarbons; 2) peroxides; 3) acids; 4) tars; 5) hydroxy acids; 6) asphaltogenes; acids; 7) asphaltenes; 8) estolides; 9) carbones and carboide.

The intermediate and final oxidation products listed here, such as tars, asphaltenes, carbonos, etc., are high-molecular-weight compounds containing oxygen, that differ in their reactions to solvents.

According to S.E. Kneyn [22] the most harmful oxidation products from the viewpoint of engine operation are the hydroxy acids and asphaltene; since they do not dissolve in oil and possess considerable viscosities, they adhere strongly to metal, clogging the ring grooves and causing burning of the piston rings.

As with any chemical reaction, the rate of oil oxidation rises with temperature. At ordinary ambient temperatures, oils oxidize extremely slowly and there is almost no oxidation at all. Thus oil may be stored in tanks of various sizes for several years. But by the time oil has reached the 50-60°C temperature of the crankcase in a working engine, the rate of oxidation has become very noticeable.

The physical state of the oil in an engine also has an effect on the rate at which it oxidizes. Oil will oxidize more slowly in a thick layer than when it is in the form of a thin oil film on the surface of lubricated parts. Under equal temperature conditions, the maximum oxidation rate should clearly occur when the oil is in a finely dispersed condition, in the form of an oil spray, when it will have maximum contact with the oxygen of the air. As a result, after 100-200 hours of engine operation, the oil performance characteristics differ considerably from those of fresh oil (increased acidity, mechanical impurities, etc.), and varnish films and carbon are deposited on the very hot surfaces of pistons, ring grooves, and piston rings, i.e., strong oxidation and polymerization of the oil occurs with the formation of asphaltenes, hydroxy acid polymers, etc.

When this happens, a certain amount of the oil, entering the highest-temperature zone (the piston head above the first ring and the combustion chamber), will decompose completely (the oil burns up).

Oil oxidation occurs much more vigorously in the presence of metals. Many metals, as well as their oxides and salts, act as catalysts, and considerably increase the oxidation-reaction speed. The most active oxidation catalysts are copper, lead, iron, the oxides of iron, and vanadium, and the naphthenates of metals. The action of combustion products from sulfur-bearing fuels is another factor accelerating the oxidation of lubricating oils. On the other hand, there are several cr-



ganic compounds (such as phenols, amines, phosphites, etc.) that retard the oxidation reaction rate. Such substances, introduced artificially into an oil in the form of additives, are called oxidation inhibitors or antioxidants.

It has recently been noted that radiation from radioactive sources also tend to accelerate the process of hydrocarbon oxidation [24].

In general, radioactive irradiation of hydrocarbons leads to some molecular consolidation, to polymerization processes, and to an increase in the molecular weight of the irradiated hydrocarbon. Thus, for example, when the diesel-oil fraction of petroleum is irradiated with a dose of  $5 \times 10^9$  roentgens, an increase in specific gravity from 0.84 to 0.94 was noted, while the viscosity (at  $38^\circ\text{C}$ ) rose from 2 to 50 sst.

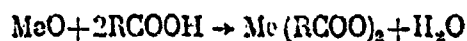
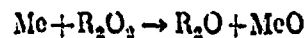
The direction taken by the change in hydrocarbon structure produced by radiation depends to a considerable degree on the dose and the nature of the irradiation.

The maximum dose of irradiation that leaves no noticeable changes in the basic properties of the oil (for example, that does not change viscosity) is  $1-2 \times 10^8$  roentgens [51].

Corrosiveness of base oils. Corrosion is the name given to the destruction of a metal that is caused by the surrounding medium. In the majority of cases, corrosion is the basic factor responsible for increased engine wear. The hydrocarbons making up an oil cannot by themselves cause corrosion. One of the causes for the corrosion of a metal in an oil medium is the presence and further generation of various oxidation products - peroxides, organic acids, etc., which react with the metal. Another factor responsible for engine corrosion is the appearance of combustion products from a sulfur-bearing fuel in the oil. As we have already noted, the first intermediate oxidation prod-

ucts are peroxides.

According to Denison, in the first stage of the corrosion process, a peroxide reacts with the metal to form an oxide of the metal, which then reacts with an acid to give a solvent:



where Me is the metal,  $\text{R}_2\text{O}_2$  the peroxide, and  $\text{RCOOH}$  an organic acid. Denison, working with white (highly purified) oils has shown that the rate of corrosion increases with the amount of peroxide contained in the oil.

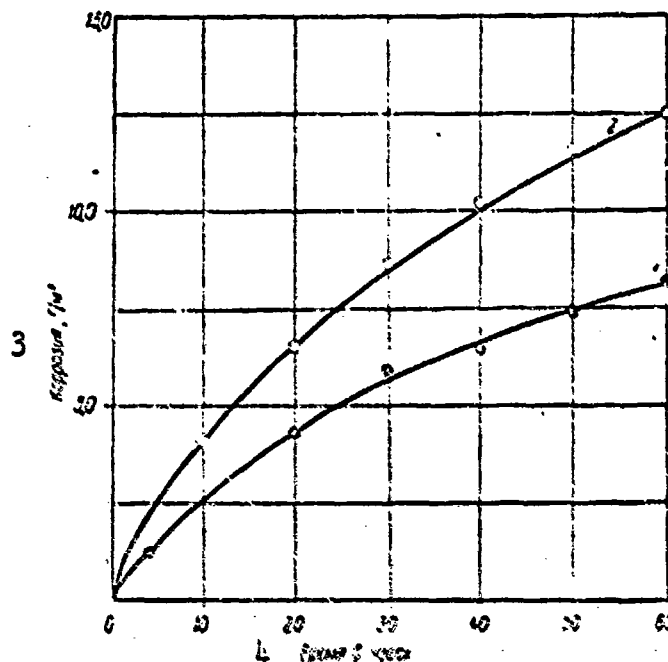


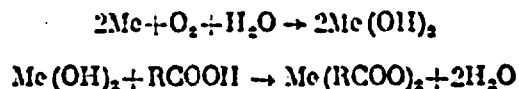
Fig. 4. Effect of water content of D-11 oil on corrosion of lead at temperature of  $80^\circ\text{C}$ . 1) Oil without water; 2) oil + 0.5% water; 3) corrosion,  $\text{g}/\text{m}^2$ ; 4) time in hours.

Thus, metal can corrode in the absence of atmospheric oxygen, provided that the oil contains, in addition to acids, peroxides and other unstable oxidation products that can yield oxygen.

Thus, for example, Prutton and Day have shown that corrosion of lead will occur in a mixture of quinone and dodecanoic acid in the ab-

sence of atmospheric oxygen.

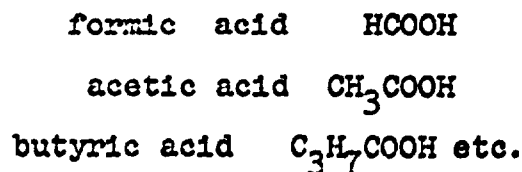
According to N.I. Chernozhukov [50], organic acids react basically with the hydrate of the metallic oxide, which forms owing to the reaction of atmospheric oxygen and water that enters the oil from without, or that forms as a result of oxidation



It follows from the corrosion-mechanism schemes considered that the presence of acids in an oil is of great importance for the process of engine corrosion.

In the majority of cases, elevated oil acidity corresponds to great corrosiveness.

All the same, the acid number cannot be used as a criterion of oil corrosiveness, since the structure of the organic acids formed in the oil is the decisive factor. The studies of B.V. Losikov [50] have shown that the corrosive action of organic acids decreases as their molecular weight increases, i.e., in order of increasing corrosiveness, the acids form the following series:



The acid numbers of fresh diesel oils normally do not exceed 0.15-0.20 mg KOH per g of oil, but the acidity of oils increases rapidly as the engine operates, reaching values of 1.5-2.0 mg KOH. According to B.V. Losikov, oils with acid numbers of up to 1.5 mg KOH, in the absence of water, have little effect on steel or iron, but acid numbers of the order of 0.5-0.6 mg KOH prove sufficient for the removal of lead from bearing alloys.

Thus, lead and its alloys are materials that are extremely liable

to corrosion due to oil oxidation products. The presence of water in an oil greatly intensifies the corrosion of alloys with lead. Figure 4 shows the effect of oil water content on the corrosion of lead plates [32].

As a rule, residual oils are less corrosive than distillates.

Table 7 shows the corrosiveness of several specimens of base oil as compared with the acidity, measured before and after oxidation of the oil in a Pinkevich apparatus. As the data given show, the acidity bears some relationship to the corrosiveness, but upon oxidation of the oils, the increase in acid number follows different laws. As far as oils with additives are concerned, there most frequently is no relationship between corrosiveness and acid number. The acidity of an oil may increase during engine operation, while at the same time, the protective film formed by the additive will protect the metal against corrosion.

The corrosion mechanism discussed above applies primarily to bearing alloys. A very pronounced corrosive-wear process occurs, however, when an engine is operated on a sulfur-bearing fuel [30]. When a sulfur-bearing fuel burns, the acidic oxides  $\text{SO}_2$  and  $\text{SO}_3$  form; they condense together with water vapor on the cooled walls of the cylinder barrel and produce sulfuric and sulfurous acids. The traces of acid, penetrating within the oil film covering the rubbing surfaces of the barrel, piston, and piston rings, are responsible for vigorous electrochemical corrosion that results in a considerable increase in the wear on rubbing parts. When an engine is operated on a sulfur-bearing fuel, there is a stronger increase in oil acidity, and water-soluble acids may also be found in the crankcase oil.

Figure 5 shows the increase in oil acidity during operation of an engine with fuels containing various amounts of sulfur. Here an in-

TABLE 7. Corrosiveness of Some Base Oils (Without Additives)

1 Наименование масла	2 Коррозионность, по Пинкевичу, г/м <sup>2</sup>		3 Кислотное число, мг KOH на 1 г масла	
	4 на чугуне	5 на свин- цово- бронзе	6 до окис- ления	7 после окисле- ния
8 Авиамасло МК-22	2,0	0,7	0,05	0,17
9 Дизельное масло ДС-11 (из серни- стых нефтей)	8,2	1,6	0,05	0,13
10 Авиамасло МС-14	45,2	15,0	0,08	0,14
11 Дизельное масло Д-11 (смесь МК-22 и СУ)	67,3	30,0	0,06	0,19
12 Машинное СУ	82,8	27,1	0,14	0,55
13 Автом АК-10	83,8	20,0	0,19	0,76
14 Дизельное масло Д-11 (из эмбен- ских нефтей)	108,0	37,0	0,42	0,50

1) Name of oil; 2) Pinkevich corrosiveness, g/m<sup>2</sup>; 3) acid number, mg KOH per g of oil; 4) lead; 5) lead bronze; 6) before oxidation; 7) after oxidation; 8) MG-22 aviation oil; 9) DS-11 diesel oil (from sulfur-bearing crudes); 10) MS-14 aviation oil; 11) D-11 diesel oil (mixture of MK-22 and SU); 12) SU machine oil; 13) AK-10 motor oil; 14) D-11 diesel oil (from Emba crudes).

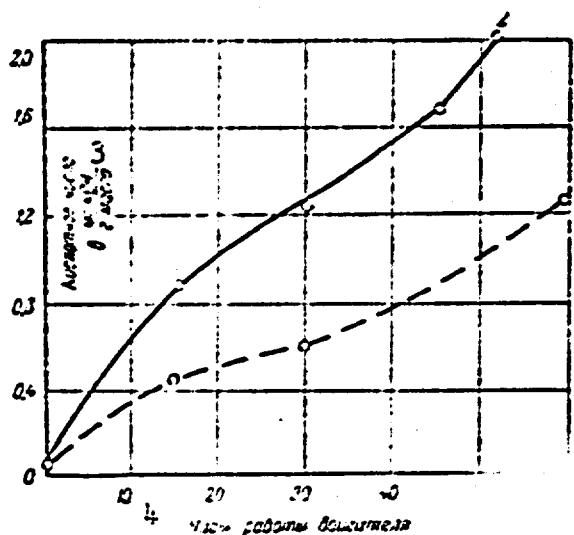


Fig. 5. Change in acidity of D-11 diesel oil during engine operation with fuels of various sulfur contents. 1) Oil acid number during operation with fuel containing 1.0% sulfur; 2) the same, with 1.6% sulfur content; 3) acid number in mg KOH/g oil; 4) hours of engine operation.

crease in carbon formation also occurs, and the carbon, which includes products of the thermal decomposition of the sulfur compounds, becomes denser and intensifies abrasive wear on the engine.

When the engine is operated on a low-sulfur fuel, an oil containing only anticorrosion additives of the AzNII-TsIATIM-1 type may be used to protect the bearing linings, which are of lead bronze. Where sulfur-bearing fuels are used, it is necessary to employ more effective additives of the alkali type, which have good detergent properties, and which are able to neutralize the acid fuel combustion products.

Carbon formation. The oxidation and thermal decomposition of the hydrocarbons in the fuel and oil in the high-temperature zones are responsible for the formation of carbon in an engine.

Carbon in the engine combustion chamber, on the piston crown, on valves, and in the exhaust system are due chiefly to incomplete combustion of the fuel. Carbon and varnish on the side piston wall, in the region of the ring channels, and on the piston skirt forms primarily as a result of the oxidation and thermal decomposition of the lubricating oil.

The mechanism by which carbon forms in an engine has been studied in detail by K.K. Papok [29]. Carbon is deposited on the piston crown owing to the presence of a low-temperature zone at the piston crown; carbon also forms in this zone owing to incomplete combustion of the fuel. Here the thickness of the carbon on the piston crown does not depend on the duration of engine operation, but is determined primarily by the temperature and by fuel quality.

Varnish and carbon formation may result in several undesirable consequences to engine operation, e.g.:

a) the loss of mobility or complete burning out of piston rings,

leading to increased losses due to friction, a loss in compression, and possible scoring of the sleeve;

b) a decrease in the effective cross sections of the scavenging and exhaust ports (in two-cycle diesels), reducing the completeness of scavenging, and leading to a drop in engine power. Figure 6 gives views of exhaust ports for a 2D100 engine following operation with a low-sulfur and high-sulfur fuel and an oil with an ineffective additive [18];

c) increased wear on rubbing surfaces of the cylinder-piston system;

d) decreased piston thermal conductivity and increased temperature, which may cause the pistons to burn out;

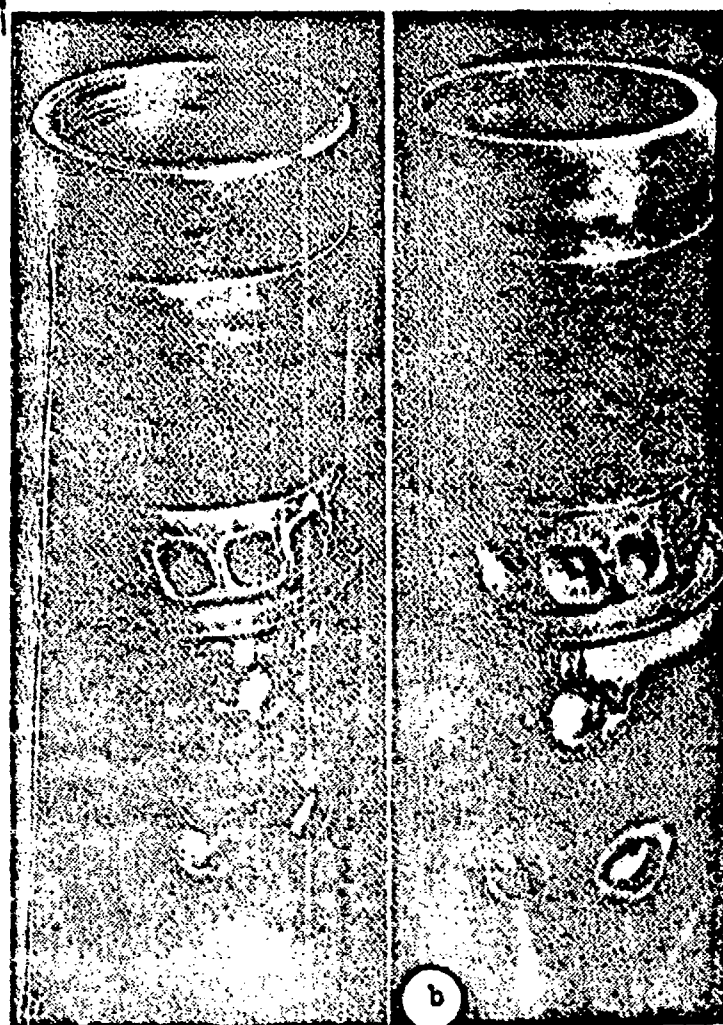


Fig. 6. Exhaust ports in barrel of 2D100 diesel. a) Following operation

on low-sulfur fuel; b) following operation on high-sulfur fuel.

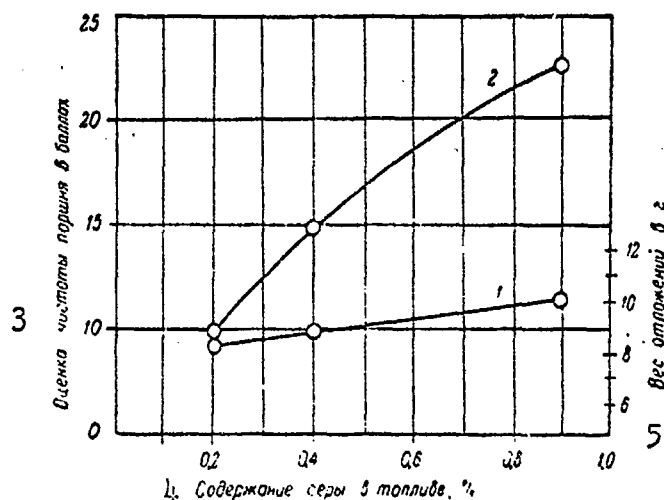


Fig. 7. Effect of fuel sulfur content on fouling evaluation and quantity of deposits on piston and rings of UIM-NATI installation. 1) Weight of deposits; 2) evaluation of nature of deposits, arbitrary units; 3) evaluation of piston cleanliness, arbitrary units; 4) fuel sulfur content, %; 5) weight of deposits, g.

TABLE 8. Effect of Fuel Sulfur Content on Carbon Properties (After Breze and Wilson)

1 Содержание серы в топливе, %	2 Содержание серы в нагаре, %	3 Плотность нагара, г/см <sup>3</sup>
0.08 1.5	1.0 9.0	0.08 0.5

1) Fuel sulfur content, %; 2) carbon-deposit sulfur content, %; 3) density of carbon deposit, g/cm<sup>3</sup>.

e) accelerated contamination of lubricating oil, filters, and oil lines.

As we have already noted, the formation of deposits on piston rings and grooves is due chiefly to the lubricating oil; fuel quality, however, has a large influence on the amount and nature of deposits.

It is known, for example, that when an engine is converted to or-



erate on gaseous fuel, so that more perfect mixture formation occurs, the quantity of ring-groove deposits decreases.

The utilization of high-sulfur fuels increases the total amount of carbon and of deposits and changes the actual nature of the carbon particles, making them denser and harder.

Figure 7 shows the variation in the amount and nature of deposits on the piston of a UIM-NATI apparatus operated with fuels of differing sulfur content [49]. In going from a fuel containing 0.2% sulfur to a fuel with a 0.93% sulfur content, the total quantity of deposits on the piston and rings rose from 7.7 to 10.7 g, while the total piston fouling evaluation (on the NATI scale) rose from 9 to 22 units.

An increase in sulfur content affects not only the amount of deposits, but also changes their properties, resulting in denser carbon deposits, more difficult to remain (Table 8). According to the data of Breze and Wilson, sulfur is absorbed by the carbon, and as a result it becomes harder and increases the abrasive wear on the engine.

TABLE 9. Change in Some Characteristics of D-11 Diesel Oil with Introduction of Additives

1 Показатели	2 Без при- савки	3% ТСИАТИМ-339 3	6% ТСИАТИМ-339 3	8% ВНИИ НП-360 4
5 Зольность, % . . .	0.01	0.33	0.71	1.10
6 Комусность, % . . .	0.25	0.66	1.2	1.6
7 Механические при- мески, % . . . . .	0.02	0.03	0.04	0.04
8 Моющие свойства по ИЗР, баллы	3.5-4.0	3.0	1.5	0.5

1) Characteristic; 2) no additives; 3) TsiATIM-339; 4) VNIИ NP-360; 5) ash, %; 6) carbon residue, %; 7) mechanical impurities, %; 8) detergent properties, PZV scale.

According to Lin's data, carbon particles formed on combustion of a heavy sulfur-bearing fuel are characterized by considerable hardness, reaching a Brinell value of 500, and have a high vanadium con-

tent. This fact made it possible for Lin to propose that engine wear is abrasive in nature when the engine uses a heavy fuel, thus contradicting the commonly held corrosion theory of wear.

Carbon scale taken from a piston crown and from piston rings following operation of an engine with a sulfur-bearing fuel normally contains from 1.0 to 2.5% sulfur. The sulfur entering into the composition of the carbon scale is found combined only in the form of complex organic compounds, or as sulfates.

According to Denison and Kavan [11] the sulfuric acid formed owing to combustion of a sulfur-bearing fuel, reacts with the oil in the upper piston-ring zone, which leads to the formation of several organic compounds containing sulfur. At the same time, some of the sulfuric acid condenses on the cylinder walls and attacks the metal surfaces of component parts, forming ferric sulfate, some of which goes into the carbon scale.

If the oil contains an alkali additive of the barium alkyl phenolate or calcium alkyl phenolate type, most of the sulfuric acid will combine to form barium (calcium) sulfate, which remains dispersed in the oil, and eventually is trapped at the oil filters; this decreases the sulfur available to participate in the formation of deposits on the piston.

Thus the most common and best-tested method of preventing carbon-deposit formation in an engine working on heavy or sulfur-bearing fuels is the introduction of detergent oil additives.

The oil carbon residue serves as a useful index in checking the quality of a crude and the degree of refining. The carbon residue, however, cannot be used to characterize the tendency of an oil to form carbon, since many data point to the absence of a direct connection between the carbon residue and the quantity of carbon deposits on a

piston.

The carbon residue is several times greater for an oil with a detergent additive than for the base oil. In this case, however, the actual tendency of the oil to form carbon and varnish on an engine piston is inversely proportional to the carbon residue. The PZV (Papoz-Zarubin-Vipper) method, developed by K.K. Papok, gives the best picture of the behavior of an oil in an engine from the viewpoint of evaluating carbon-forming tendencies and detergent properties of oils with additives (Table 9).

The ash and mechanical-impurity contents of an oil also serve as indices characterizing the degree of refining and the absence of contaminants under storage and transportation conditions.

The ash content characterizes primarily the presence or absence of additives in the oil, and the amount of ash gives us some rough idea as to the additive concentration.

In the overwhelming majority of cases, modern multipurpose additives are organometallic compounds, and the introduction of an additive of the TsIATIM-339 type, as the tabular data show, has a strong effect on the ash content.

#### VARIETY AND GRADES OF OILS USED FOR DIESEL LUBRICATION

The basic grades of oils used to lubricate high-speed diesel engines are the diesel oils produced in accordance with GOST 5304-54 and 6581-57.

GOST 5304-54 diesel oils are made from distillates, or are obtained by blending residuals and distillates obtained during the processing of oily low-sulfur petroleum.

Thus, for example, D-11 diesel oil may be manufactured by burning 70% SU GOST 1707-51 machine oil with 30% MK-22 GOST 1013-49 aviation oil. Diesel oils manufactured to this standard are also made with ad-

ditives (Dp-14, Dp-11, and Dp-8 oils), and without additives (D-11 oil). Types Dp-14, Dp-11, and Dp-8 oils contain 3% TsIATIM-339 or AzNII-TsIATIM-1 additive. Engines operated with a diesel fuel containing more than 0.2% sulfur should use only an oil with TsIATIM-339 additive or other, more effective additive. Oils with the AzNII-TsIATIM-1 anticorrosion additive may be used in diesels with lead-bronze bearings run on a low-sulfur fuel.

Type Dp-11 oil is the basic grade of oil used for high-speed diesels.

Type Dp-8 oil is used during the winter in automotive and mobile diesels operating out of doors. Type Dp-14 oil is a summer grade designed for use in diesel locomotives, tractors, and other diesel engines operating in areas with high ambient temperatures.

In view of our limited reserves of low-sulfur petroleum, production of DSp-11 GOST 6581-57 diesel oil from sulfur-bearing crudes has begun.

Type DSp-11 oil is produced presently only with the TsIATIM-339 additive; in the near future, however, we may expect expanded production of diesel oils using more effective additive (VNII NP-360, etc.).

High-viscosity, aircraft (GOST 1013-49 and 9320-60), and special MT (GOST 6360-58) oils are used to lubricate certain types of high-combustion-intensity diesels with high piston speeds (for example M-50 and D6 motors, etc.).

Types MK-22, MS-24, MS-20, MS-14, and GOST 1013-49 aviation oils are high-grade oils obtained during processing of selected low-sulfur petroleums; intense sulfuric-acid or solvent refining is used. Although, as we have said, the basic function of these oils is the lubrication of piston aircraft engines, they are also used for certain surface and marine engines. Aviation oils are produced without addi-

tives. Additives may be introduced into the oil on the customer's special order.

In order to expand reserves available for the production of aircraft oils, tests are presently being carried out and production being set up for certain grades of oils obtained by refining sulfur-bearing crudes (such as MS-20S oil, GOST 9320-60).

MT (MT-16p and MT-14p), GOST 6360-58 oils are designed for lubrication of special diesel engines. MT-16 oil is produced with 3-4% of TsiATIM-339 additive and 0.3% AzNII-TsiATIM-1 additive.

Type MT-14p oil is produced from a low-viscosity base by using polyisobutylene as a thickening agent; this results in a flat viscosity curve (see Fig. 3), i.e., relatively low viscosity at low temperatures, which improves lubrication and aids engine starting under winter conditions. This oil is presently produced with AzNII-TsiATIM-1 additive, and is designed for lubrication of diesel engines using low-sulfur fuels.

Oil for low-speed diesels (motor oil) (GOST 1519-42) is a distillate produced by acid-mechanical refining and is considerably better than diesel oils with respect to carbon-forming tendencies and anti-corrosion properties.

In the actual operation of low-speed diesels, motor oil is frequently replaced with AKp-10, ASp-10, and AK-15 (GOST 1862-60) "avtol" type motor oils.

The basic indices characterizing the physicochemical properties of commercial domestic oils used for diesel lubrication are shown in Table 10.

Utilizing oils from sulfur-bearing petroleums. During the course of the seven-year plan (1959-1965), the capacity for production of lubricating oils should double.

In order to satisfy the rising requirements for oils, as in the case of fuels, a heavy commitment to the processing of sulfur-bearing crudes from Eastern fields is necessary.

Although, before, the need for oils was satisfied primarily by refining crudes from Baku and other Southern areas, facilities have recently been set up to produce several aviation, diesel, and automotive oils by processing Eastern crudes. The output of Baku oils presently amounts to no more than 50% of the total lubricating-oil production. Lubricating oils obtained by refining sulfur-bearing crudes from Eastern fields differ from Baku oils in hydrocarbon-group composition, and are higher in sulfur content. Thus, DS-11 diesel oil (from Eastern crudes) contains up to 1.0% sulfur as against 0.2-0.3% for D-11 Baku oil.

As in the case of fuels, the presence of sulfur compounds in the oil affects the condition of the engine. In this case, however, we are not concerned with acid corrosion, since the quantity of combustion products due to sulfur compounds in the oil that form when the oil burns is very small in comparison with the quantity of fuel combustion products. By themselves, the sulfur compounds contained in oil not only do not cause corrosion, but, on the contrary, increase the anti-wear qualities of the oil, acting, as it were, as natural additives.

Oils from Eastern sulfur-bearing crudes also have better viscosity-temperature properties than the corresponding Baku oils; they are, however, characterized by a great tendency to oxidation and, consequently, to carbon formation.

Oxidation of oils produced from Eastern crudes produces considerably more gum and asphaltene. Table 11 gives some data due to N.G. Pucikov and his associates [35] obtained by oxidizing various oils in a EX-2 apparatus.

TABLE 10. Basic Quality Indices for Domestic Oils Used for Diesel Lubrication

1 Показатели	2 Авиационные масла				4 Специальные масла (MT)	
	3 ГОСТ 1013-49			3 ГОСТ 9320-60	3 ГОСТ 6300-58	
	11C-22	6C-20	8C-14	9 MC-20C	10-10n MT-10n	10 MT-15n
19 Вязкость кинематическая при 100°С, сст	18 Не менее 22	20	14	18 Не менее 20	32 В пределах 16,0—17,5	13,5—14,5
20 Отношение кинематической вязкости при 50° к кинематической вязкости при 100°С, не более	8,75	7,85	6,65	7,6	7	4
21 Зольность, %, для масла:						
22 без присадок, не более	0,004	0,003	0,003	0,003	—	—
23 с присадкой ЦИАТИМ-339, не менее	—	—	—	—	0,25	0,13
25 Коксуемость, %, не более (до добавления присадки)	0,7	0,3	0,45	0,45	0,30	0,20
26 Кислотное число, мг KOH на 1 г масла:						
27 без присадки, не более	0,1	0,05	0,25	0,05	—	—
28 с присадкой, не более	—	—	—	—	0,15	0,10
29 Температура застывания, °С, не выше	-14	-18	-30	-18	-25	-43
30 Коррозионность на пластинках из свинца марки С1 или С2, г/м², не более	20	45	60	15	10	10
31 Термоокислительная стабильность по методу Папок при 250°С, мин, не менее	35	17	20	17	—	25

1) Index; 2) aviation oils; 3) GOST; 4) special oils (MT); 5) diesel oils; 6) motor-tractor oils; 7) motor oils; 8) MS; 9) MS-20S; 10) MT-16p; 11) Dp; 12) D; 13) DSp; 14) ML2-V; 15) VTU NP; 16) GOST 1862-60, no additives; 17) VTU22-58 with TsIATIM-339 additive; 18) no less than; 19) kinematic viscosity at 100°C, sst; 20) ratio of kinematic viscosity at 50° to kinematic viscosity at 100°C, no more than; 21) ash, %, for oil; 22) without additive, no more than; 23) with TsIATIM-339 additive, no less than; 24) VNII NP-360 additive; 25) carbon residue, %; no more than (prior to introduction of additive); 26) acid number, mg KOH per 1 g of oil; 27) without additive, no more than; 28) with additive, no more than; 29) pour point, °C, no more than; 30) corrosiveness with strips of Types S1 and S2 lead, g/m², no more than; 31) thermal oxidation stability, Papok method, at 250°C, min, no less than; 32) in the range from; 33) at.

5 Дизельные масла							Автотракторные масла 6		Моторное масло 7	
ГОСТ 5304-54				ГОСТ 8581-57	ВТУ НИИ 23-58	ВТУ НИИ 80-60	ГОСТ 1862-57		ГОСТ 1862-57 без присадки	ВТУ 22-58 с присадкой ЦИАТИМ-339
11-14 Д-14	11-11 Д-11	11-8 Д-8	11-8 Д-8	13 Д-11	13 Д-8	14 М-2-В	АК-15	АК-10	ГОСТ 1862-57 без присадки	ВТУ 22-58 с присадкой ЦИАТИМ-339
32 В пределах 13,5-15,5				8-9 10,5-11,5	8,2-8,5	12	18 Не менее 15	10	33 При 50°С 62-68	33 При 50°С 62-68
7,75	6,5	7,3	6,0	6,0	5,5	6,2	9,0	7,0	—	—
—	—	0,005	—	—	0,01	0,005	0,014	0,015	0,04	0,04
0,25	0,25	—	0,25	0,25	0,3	1,0 С присадкой ВНИИ НП-360	—	—	—	0,22
0,55	0,4	0,4	0,2	0,3	0,15	0,3	0,70	0,40	0,4	0,4
—	—	0,15	—	—	0,02	0,02	—	—	—	—
0,10	0,10	—	0,10	0,02	—	—	0,20	0,15	—	0
-10	-15	-18	-25	-15	-25	-15	-5	-25	0	—
13	13	—	13	10	10	10	—	—	—	—
25	20	—	20	—	—	—	—	—	—	—



In this case, the oxidation of the Eastern oils is different in nature, and the accumulation of large quantities of gum and asphaltenes facilitates the formation of tacky residues, which are responsible for piston-ring burning during engine operation.

Table 12 compares results of an inspection of the condition and measurement of wear for a 4Ch10.5/13 engine after 150 hours of operation with a high-sulfur fuel, using D-11 Baku diesel oil and DS-11 oil (without additives) produced from Eastern crudes.

In changing from D-11 oil to DS-11 oil, some decrease in wear of sleeves and piston rings was noticed, while at the same time there was a sharp increase in the number of burnt rings, while more varnish formed on the piston skirt.

Consequently, diesel oils made from sulfur-bearing crudes may be used in diesel engines only when they contain effective detergent additives. Thus, DS-11 diesel oil (GOST 8581-57) is supplied only as an oil with an additive, while diesel oils made from Caucasus crudes (GOST 5304-54) are produced both with and without additives.

The utilization of detergent oil additives may decrease considerably or completely eliminate carbon and varnish deposits on the pistons, but this does not mean that thermal decomposition of the oil can be avoided by this method. The thermal stability of an oil, i.e., the stability of its composition under high temperatures, is determined by the composition of the lubricant itself. All petroleum hydrocarbons contained in an oil, when subjected to temperatures of 200-250°C, i.e., temperatures occurring at the piston walls, begin to decompose and form carbon-carrying products known commonly as varnish and scale. Oil thermal stability can be increased only over a relatively small range by increasing petroleum-oil quality through improved refining methods and the utilization of additives. The increase in engine combustion in-

tensity, and plans for the creation of highly supercharged diesel engines having piston temperatures in the upper-ring region of the order of 300-350°C or more will require in individual cases the utilization of new types of lubricants with changed structures for the component molecules.

TABLE 11. Oxidation Stability of Oils in DK-2 Apparatus and Characteristics of Combustion Products

1 Масло	2 Количество осадка при окислении за 50 ч	3 Характеристика осадка	
		4 асфальтенов, %	5 карбенов и карбондов, %
6 Антол AC-5 (из сернистых нефтей) . . . . .	8,1	100	Следы 11
7 Антол AC-6 (бэкинский) . . . . .	5,3	50	50
8 Машинное СУ . . . . .	7,3	50	50
9 Масло SAE-20 HD . . . . .		Отсутствует 10	

1) Oil; 2) quantity of residue, 50-hour oxidation; 3) residue characteristics; 4) asphaltenes, %; 5) carbenes and carboids, %; 6) AS-5 motor oil (sulfur-bearing crudes); 7) AS-6 motor oil (Baku); 8) SU machine oil; 9) SAE-20 HD oil; 10) none; 11) traces.

TABLE 12. Comparison of Conditions of 4Ch10.5/13 Engine After Operation with D-11 (Baku) Oil and DS-11 (Sulfur-Bearing Crudes) Oil Without Additives

1 Наименование замеров	2 Значения замеров, полученных после 150 час работы двигателя на масле	
	3 D-11	4 DS-11
Износ		
6 Износ всех поршневых колец, е . . . . .	1,00	0,81
7 То же, % . . . . .	100	75
8 Износ гильзы цилиндра . . . . .	58	41
9 То же, % . . . . .	100	70
10 Общий износ по содержанию железа в масле, е . . . . .	7,2	4,4
11 То же, % . . . . .	100	61
10 Нарастание образования		
Количество пригрезших колец, шт. 11	1	6
Площадь износа поршня, покрытая лаком, % . . . . . 12	30-40	60

1) Measurement; 2) measurement values after 150 hours of engine operation with oil; 3) D-11; 4) DS-11; 5) wear; 6) wear on all piston rings,

g; 7) the same, %; 8) wear on cylinder skirt; 9) total wear in terms of iron content, g; 10) carbon formation; 11) number of burnt rings; 12) piston-skirt surface covered with varnish, %.

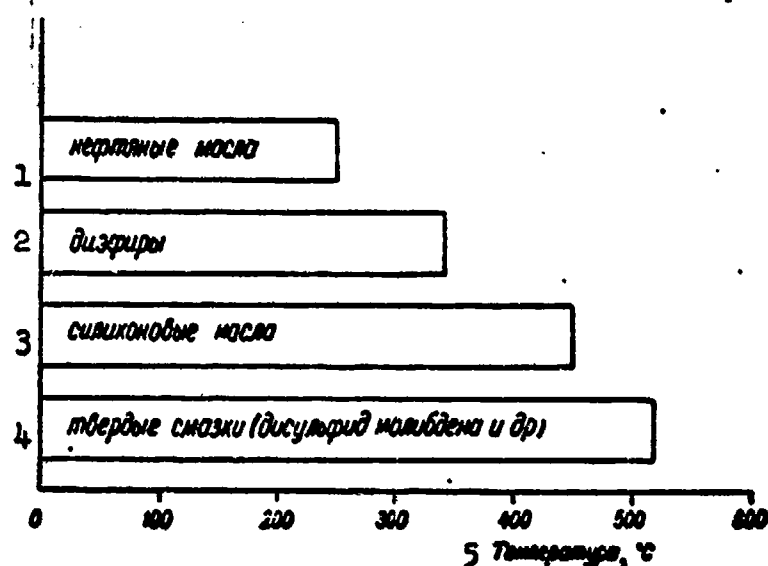


Fig. 8. Temperature ranges over which various lubricants can be used. 1) Petroleum oils; 2) diesters; 3) silicon oils; 4) solid lubricants (molybdenum disulfide, etc.); 5) temperature, °C.

Considerably greater thermal stability (Fig. 8) is displayed by various synthetic oils (oils based on diesters, fluorocarbons, and silicon oils); they are still limited in application, but there is no doubt that they will become more common in the future.

Foreign oil classification. Foreign motor oils are classified into the following groups on the basis of grade and function:

a) ordinary oils, also called regular and premium grades, that do not contain additives or that contain small quantities of antioxidant additives alone. These oils are designed for carburetor-type engines and low-combustion-intensity diesels running on low-carbon fuels;

b) oils for severe operating conditions ("heavy-duty oils"), carrying the letter designation HD; they contain considerable amounts of detergent additive, and are designed for lubrication of supercharged diesels:

TABLE 13. Classification of Oils in Terms of Oil Utilization Conditions in Engine (United States)

1) Type of oil; 2) additive content; 3) antioxidant and anticorrosion, %; 4) detergent; 5) mg-mole/kg; 6) regular; 7) premium; 8) HD for severe service; 9) HD for especially severe service; 10) series; 11) no additives; 12) up to.

1	Вязкость кинематическая при 100°С, <i>сст</i> . . . . .	18,7
2	"      "      "      при 50°С, <i>сст</i> . . . . .	116,5
3	Отношение вязкости при 50° к вязкости при 100°С . . . . .	7,8
4	Зольность, % . . . . .	3,96
5	Кислотное число, <i>мг KOH</i> на 1 <i>г</i> масла . . . . .	Шелочная реак-ция
6	Конусность, % . . . . .	5,21
7	Коррозийность, по Пинкешу, <i>с</i> <i>мг</i> : . . . . .	
8	на свинце . . . . .	21,4
9	на свинцовистой бронзе . . . . .	1,8
10	Термоокислительная стабильность по методу Панок, при 230°С, в минутах . . . . .	300

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TABLE 15. SAE Classification of Crankcase Lubricating Oils by Viscosity (United States)

1 Марка масла по классификации SAE	2 Вязкость масла при температуре							
	-17.8 (0° F)				99.8° C (210° F)			
	3 наименьшая		4 наибольшая		5 наименьшая		6 наибольшая	
	кинематическая, сст, 5	условная, °VU, 6	кинематическая, сст, 5	условная, °VU, 6	кинематическая, сст, 5	условная, °VU, 6	кинематическая, сст, 5	условная, °VU, 6
5W	—	—	874	115	—	—	—	—
10W	1307	112	2614	344	3.88	1.3	—	—
20W	2614	344	10458	1376	—	—	—	—
20	—	—	—	—	5.75	1.46	9.65	1.80
30	—	—	—	—	9.65	1.80	12.98	2.12
40	—	—	—	—	12.98	2.12	16.82	2.52
50	—	—	—	—	16.82	2.52	22.75	3.19

Notes. a) The letter W indicates winter grades of oil; b) the viscosity values given in the table make it possible to select a domestic lubricating oil that corresponds in viscosity to an imported oil, as is frequently required under practical conditions when oils are to be chosen for foreign-made engines for which the manufacturers normally recommend oils of some given class. Thus, for example, SAE-30 oil, which is used very frequently for diesel lubrication, will correspond in viscosity to D-11 or Dp-11 (GOST 8304-54) domestic diesel oils, which have a kinematic viscosity at 100° ranging from 10.5 to 12.5 sst.

1) Oil grade, SAE classification; 2) oil viscosity at temperature of; 3) minimum; 4) maximum; 5) kinematic, sst; 6) relative, °VU (Engler).

Depending on the conditions under which the oil is used in the engine (degree of supercharging, variations in conditions, fuel sulfur content, etc.), these oils are classified into series 1, 2, and 3; the specifications stipulate the particular conditions for the motor tests that the oils must pass in order to be considered suitable for service (see Chapter 3).

Table 13 shows sample additive contents used with an oil to give it the properties that permit it to be classified in one of the oil groups.

Thus, Type HD series 2 oils produced by the English Monsanto Company contains 0.7% Santolube 493 antioxidant and 9% Monte 613 detergent additive. The series 3 oils include the well-known imported Mobilguard oil. The additive content of these oils is often raised to 15-20% so that they meet the specifications for the special motor tests which they should pass.

Mobilguard oil is designed to lubricate the cylinders of high-power low-speed diesels of the Burmeister and Wain type, which use heavy sulfur-bearing fuels; they are also used for free-piston gas generators. This oil is characterized by very high ash content, alkalinity, and carbon residue (Table 14) which indicates the high additive content which reaches roughly 20-25%. The oil has good thermal stability, good detergent properties, and is able to neutralize the action of combustion products from a high-sulfur fuel. At the present time, similar oils are not being produced in this country.

Foreign oils are also produced for the market in the form of oils of differing viscosities and carry, in addition to the company names, numbers corresponding to the viscosity in accordance with the SAE classification.\* Winter grades carry the additional letter designation W. Table 15 shows the classification of oils by viscosity in SAE numbers. The basic summer grades are SAE-30 and SAE-

In addition, so-called "all-season" oils are produced abroad; they have a flat viscosity curve that ensures engine lubrication under various temperature conditions. These oils are made by thickening low-viscosity bases with high-molecular-weight compounds. All-season oils are given double numbers on the SAE scale, for example, SAE-5W/30. This means that the given oil has the same high viscosity as SAE-30 oil at high temperatures, while at low temperatures, its viscosity does not exceed the viscosity of SAE-5W winter oil. The results ob-

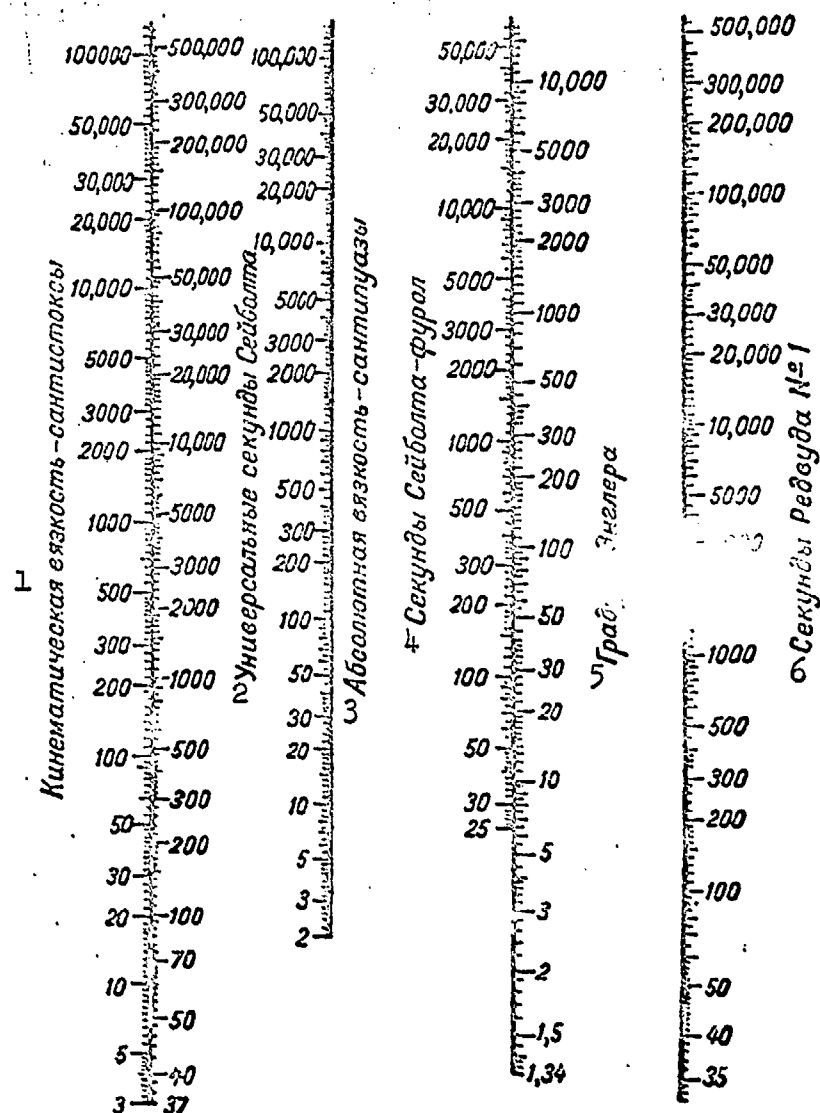


Fig. 9. Nomogram for viscosity conversion.  
 1) Kinematic viscosity, centistokes; 2) Saybolt universal seconds; 3) absolute viscosity, centipoises; 4) Saybolt-Furol seconds; 5) degrees Engler; 6) Redwood seconds, No. 1.

tained by using thickened oils are described in Chapter 2.

The relative viscosities of foreign oils are normally expressed in seconds for a Saybolt viscosimeter (United States) or a Redwood viscosimeter (Great Britain).

A nomogram (Fig. 9) can be used to convert kinematic viscosity to relative viscosity in degrees  $\nu U$  (Engler), as well as to Saybolt and Redwood seconds, and vice versa.

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[Footnotes]

- 2 K.K. Papok, Problems of Fuel and Oil Quality and Utilization at the Level of the New Goals. Chemistry and Technology of Fuels and Oils, 1959, No. 2, page 2.
- 45 SAE (Society of Automotive Engineers). This is the society of automobile-industry engineers of the United States.

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[List of Transliterated Symbols]

- 7  $\phi = f = \text{forsirovaniye} = \text{supercharging}$
- 16  $\pi_3 = p_3 = \text{puaz} = \text{poise}$



## Chapter 2

### DIESEL-OIL ADDITIVES

#### FUNCTION, COMPOSITION, AND GENERAL PROPERTIES OF OIL ADDITIVES

Additives can be classified into the following groups on the basis of their effects.

TABLE 16. Over-all Consumption of Motor-oil Additives in United States (Thousands of Tons)

1 Вид присадки	2 Годы		
	1955	1956	1960
3 Моющие (детергенты) . . . . .	124.8	131.6	149.8
4 Вязкостные . . . . .	55.8	67.2	82.2
5 Антиокислители . . . . .	31.3	33.2	35.5
6 Депрессаторы . . . . .	13.2	13.2	13.6
7 Присадки, повышающие маслянистость и противозадирные свойства	25.9	26.3	30.4
8 Всего . . .	251.0	271.5	310.5

1) Type of additive; 2) year; 3) detergent; 4) viscosity; 5) antioxidant; 6) depressant; 7) additives increasing oiliness and antiseizing properties; 8) total.

1. Detergent additives, whose function is to keep carbon particles or oil oxidation products in suspension (dispersed), thus preventing the deposition of carbon and varnish on the working surfaces of the engine.

2. Anticorrosion and antioxidant additives (inhibitors), which retard the process of oil oxidation during engine operation and protect engine parts against corrosion.

3. Viscosity additives, intended to thicken low-viscosity oils so that oils with improved viscosity-temperature properties can be ob-

tained.

4. Depressants, or additives lowering the pour point of oils.

5. Antiseizing oil additives designed to lubricate parts subjected to high mechanical loads.

Abroad, and especially in the United States, considerable volumes are involved in the production and utilization of oil additives. Thus, in the United States, the production of oil additives during 1960 reached 310.5 thousand tons (Table 16).

Of this amount, about 50% were detergents, about 20% viscosity additives, and 11% antioxidants.

It should be noted that in other countries oils designed for especially severe service conditions have additive contents reaching 10-15%, and in isolated cases even more; the average additive content of all oils produced in the United States is 4-5%.

In connection with the widespread utilization of high-sulfur fuels in diesel engines, it has become necessary to use additives, and primarily those that have good detergent and anticorrosion properties, i.e., that are able at the same time to neutralize the acid combustion products of high-sulfur fuels, retard oil-oxidation processes, thus reducing wear and corrosion and preventing the deposition of carbon scale and varnish on elements of the engine cylinder-piston system.

Thus oil additives designed to be used in diesel engines running on high-sulfur fuels are produced industrially in the form of multipurpose (complex) additives that possess detergent, antiwear, and anticorrosion properties at the same time.

For the most part, the production of multipurpose additives was set up in the USSR following the war. Such additives are AzNII-4, AzNII-TsI.TIM-1, and TsIATIM-339 additives, whose utilization represents a considerable operational contribution to increased domestic-oil qual-

ity.

At the present time, however, these additives do not completely satisfy the increasing requirements imposed by the operation of supercharged diesel engines running on high-sulfur fuel.

In accordance with the requirements of diesel-engine design, several new types of additives have been developed, tested, and readied for production; these additives are known by their numbers: AzNII-7, VNII NP-360, and MNI IP-22.

Among the Soviet scientists who have made major contributions to the synthesis and technology of domestic multipurpose oil additives are A.V. Druzhinina, V.I. Isarulyants, S.E. Kreyn, I.M. Kuliyeu, V.N. Monastyrskiy, and P.I. Sanin.

The efforts of K.K. Papok, N.G. Puchkov, B.V. Losikov, N.I. Chernozhukov, K.S. Ramayya, Ye.G. Semenido, Yu.S. Zaslavskiy, and other investigators have resulted in the further development of oil test methods and advances in the study of the mechanisms by which additives act.

TABLE 17. Basic Types of Multipurpose Diesel-Oil Additives

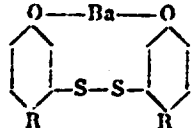
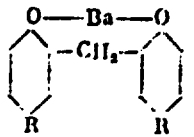
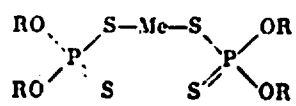
1 Тип присадки	2 Марки присадок, относящихся к данному типу	3 Схема строения основного компонента присадки
4 Алкилфенольные присадки	8 а) АЗНИИ-НИАТИМ-4 9 НИАТИМ-339 10 АЗНИИ-7  11 б) НИИИ НИ-371 12 НИИ-1	а)  б) 
5 Фосфорсодержащие присадки	13 НИИИ НИ-360 14 НИИИ НИ-22 15 АФ-1	 7 где Me - Ba, Ca, Zn

TABLE 17 (Continued)

6 Сульфонатные присадки	16 (AzNII-4)	$R-SO_2-O-Me-OH$
	17 ПМС-19	$R-SO_2-O-Me-O-SO_2-R$
	18 СБ-3	где $Me=Ba, Ca$
	19 ИГ-102	

1) Type of additive; 2) additive designations for given type; 3) structural diagram of basic additive component; 4) alkylphenol additives; 5) phosphorus-containing additives; 6) sulfonate additives; 7) where; 8) AzNII-TsIATIM-1; 9) TsIATIM-339; 10) AzNII-7; 11) VNII NP-371; 12) BFK-1; 13) VNII NP-360; 14) MNI IP-22; 15) DF-1; 16) (AzNII-4); 17) PMS-19; 18) SB-3; 19) NG-102.

Many scientific research institutes, petroleum refineries, diesel-manufacturing plants, and organizations operating engines have participated in motor tests of new grades of oils and of additives, and in their introduction into industry and application.

There are two approaches to the synthesis of multipurpose oil additives: the creation of additives consisting basically of a single chemical compound that possesses various functional properties, and the development of multicomponent blended additives in which the properties of one component compensate for inadequate properties of another.

The TsIATIM-339, AzNII-7, MNI-22, etc., additives are of the first type.

The second group includes the blended additives that are so common at present and which are mixtures of two components, for example, the VNII NP-360, AzNII-8 additives, and others. If certain required properties are poorly represented in a given multipurpose additive, a blended additive is formulated; here the inadequate properties of one component are compensated by the addition of another component to the additive.

Thus, for example, VNII NP-360 additive is a mixture of VNII NP-

350 detergent component (barium alkyl phenolate) and a component consisting of VNII NP-354 (zinc dialkylphenyl dithiophosphate), which has good neutralizing and antiwear properties.

In addition, several experimental additive types have been developed, which have been assigned the numbers DF-1, PMS-19, SB-3, VFK-1, VNII NP-370, MDS, ZIT, etc.; they have been mixed with various antioxidants. Many of these additives have undergone laboratory and bench tests, and are presently being introduced on an industrial basis.

Viscosity additives and depressants, whose use is dictated not by engine combustion intensity or fuel quality, but by base-oil properties and climatic operating conditions, are produced as additives with a specific function.

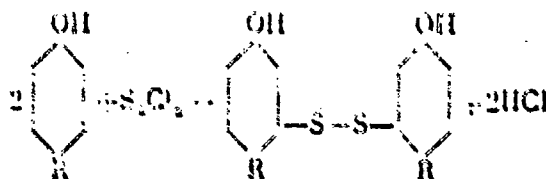
Multipurpose oil additives may be classified on the basis of structure into the following main groups.

1. Alkylphenol additives.
2. Phosphorus-containing additives.
3. Sulfonate additives.
4. Blended additives and others.

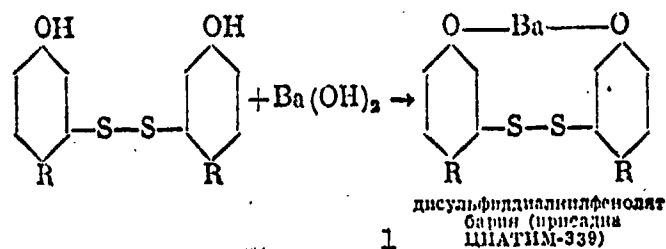
Table 17 shows the structure of the basic additive types.

Alkylphenol additives (TsiATIM-339, AzNII-7) are presently the main additive types. They are sulfurized barium or calcium alkylphenolates.

Type TsiATIM-339 additive is manufactured by reacting an alkylphenol with sulfur monochloride:



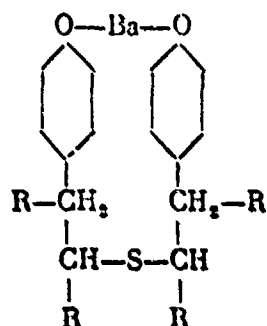
with the resulting disulfide being treated with barium hydroxide:



1) Barium disulfide dialkylphenolate (TsIATIM-339 additive).

where R is a hydrocarbon radical (alkyl) with 8 to 12 carbon atoms.

The TsIATIM-339 and AzNII-7 alkylphenol additives differ in structure in the length of the hydrocarbon chain in the radical (R) and in the position of the sulfur atom, owing to differences in the processes used to produce the additives [25]. During manufacture of AzNII-7 additive, the phenol is first alkylated with sulfurized alkene hydrocarbons; as a result, the sulfur is located in the side radicals R. The structure of AzNII-7 additive is as follows [25]

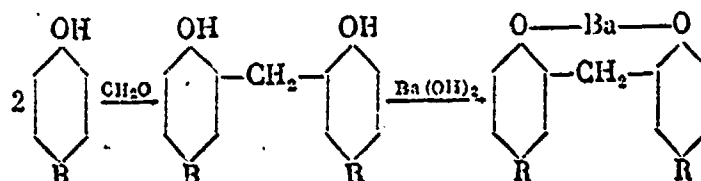


The structural formulas given in Table 17 show only the structural diagrams of the basic additive component, as an example. Commercial multipurpose additives very frequently are mixtures of several components whose structure does not always correspond to the specific stoichiometric proportions. Thus, for example, TsIATIM-339 commercial additive is made up of a sulfur-containing alkylphenol (up to 23%), sulfur-containing barium alkylphenolate (up to 25%), and about 50% spindle oil, used as a thinner, and certain other admixtures [1].

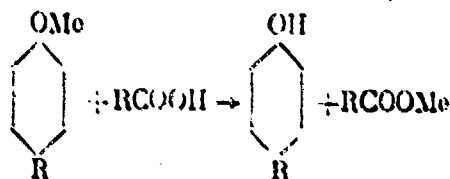
The so-called completely substituted TsIATIM-339p additive (with

100% substitution of barium for the hydroxyl hydrogen) has somewhat better detergent and anticorrosion properties.

Another type of alkylphenol additive that has recently been developed is obtained by condensation of alkylphenols with formaldehyde, followed by saponification of the condensation product with barium or calcium hydroxide (BFK-1, VNII NP-370, VNII NP-371 additives) in accordance with the following diagram



As with the alkylphenols, the alkyl phenolates are capable of entering into exchange reactions in the presence of even weak organic acids; they combine with the acid in the form of the corresponding salt in accordance with the following diagram:



The detergent properties of alkylphenol additives [14] lead to:

- a) neutralization of the acid products that form in the oil during its oxidation or as a result of the action of combustion products from a high-sulfur fuel;
- b) increased solubility of asphalt-tar materials that form in the oil; they are prevented from coagulating (dispersing action of the additive).

Thus, the basis for TsIKIM-339 additive is barium alkyl phenolate (APB), which imparts detergent and neutralizing properties to the oil with additive. Thus, APB may be used as a detergent component in formulating other additives. Sulfur atoms are introduced into the APB

molecule in order to impart anticorrosion properties, i.e., to create a multipurpose additive.

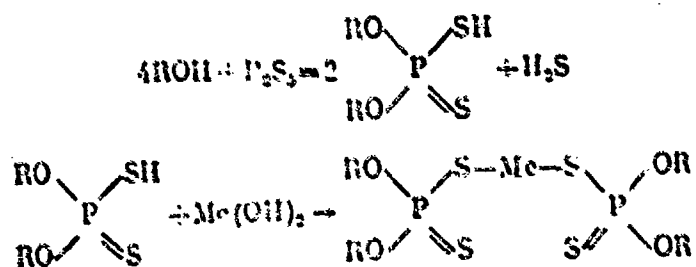
The oils produced by the petroleum industry normally contain 3% TsIATIM-339 additive. According to the data of N.G. Puchkov and his associates [37] when the fuel sulfur content exceeds 1.0%, it is desirable to increase the content of TsIATIM-339 additive to 5%; a further increase in additive concentration, however, does not produce a proportional decrease in engine wear, and does not make it possible to obtain the values reached when the engine is run on a low-sulfur fuel (see Fig. 26).

Phosphorus-containing additives. These additives include the VNII NP-360, MNI IP-22, DF-1, and other additives. These additives are based on alkyl- or arylidithiophosphates, i.e., salts of esters of dithiophosphoric acid or mixtures of compounds of this type with other components.

As we have already mentioned, VNII NP-360 additive is a mixture of components: VNII NP-350 (barium alkyl phenolate) and VNII NP-354 (a zinc salt of dialkylphenyldithiophosphoric acid)



The VNII NP-354 component is obtained by reacting alkylphenol with phosphorus pentasulfide and then refining the resulting dialkylphenyldithiophosphoric acid and obtaining its zinc salt. It may be assumed that the synthesis reaction for this additive follows the following scheme





where R is an alkyl or aryl radical.

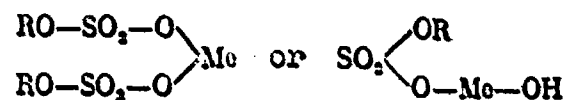
The negative factor in the production of phosphorus-containing additives is the fact that phosphorus pentasulfide is a somewhat scarce material; at present, this limits any broad-scale commercial production of additives of this type [38].

The VNII NP-360 additive has good detergent and antiwear properties.

The MNI IP-22 additive is calcium salt of dithiophosphoric acid diester of similar structure.

Additives of the DF type (dialkyldithiophosphates) are also organophosphorus compounds and differ from the VNII NP-354 component in the length of the hydrocarbon chain in the radical R, and in the production technology [40].

Sulfonate additives take the form of barium or calcium salts of sulfo acids, obtained by sulfurizing petroleum fractions. Metal sulfonates may have the following structure



In addition, sulfonates are known that contain a considerably greater amount of metal than is provided for by the stoichiometric proportions in accordance with the formulas given.

In many cases, the metal content may be 8-10 times that required from the stoichiometric relationships.

Such sulfonate additives, which are characterized by high ash content, are called "multiash."

Type PMS-19 multiash additive is a calcium sulfonate with an ash content of about 19%. It is manufactured on the basis of sulfo acids obtained from a high-sulfur crude (As-5 AK NPZ oil) by sulfurizing together with concentrated sulfuric acid, fuming sulfuric acid, or gas-

eous  $\text{SO}_2$ , followed by treatment with calcium oxide [2].

A similar additive, made by the Yaroslavl' petroleum refinery, using perfume-oil wastes has been given the designation PMS-Ya.

The NG-102 additive also is a calcium sulfonate, and differs from PMS-19 additive in the production technology used.

The SB-3 additive is a barium sulfonate based on sulfo acid obtained by sulfurization of D-11 diesel oil.

Recently, blended additives have come to be formulated; they are made up of additives of differing structures.

Thus, for example, NG-102u (improved) additive is made by blending 90% NG-102 sulfonate additive with 10% VNII NP-370 alkylphenol additive.

The VNIINP-362 additive consists of a mixture of the sulfonate PMS-19 with barium alkyl phenolate in 1:1 proportions.

In addition to the types of additives listed above, which contain barium, calcium, zinc, or some other metal, there are also the well-known "ashless additives," which do not contain metals, but are based on products of the polymerization of esters of polyatomic alcohols and derivative alkylamines. Thus, for example, according to foreign data [23] good detergent and antiwear qualities are characteristic of the copolymer of lauryl methacrylate and diethylamino ethylmethacrylate, which has the following structure

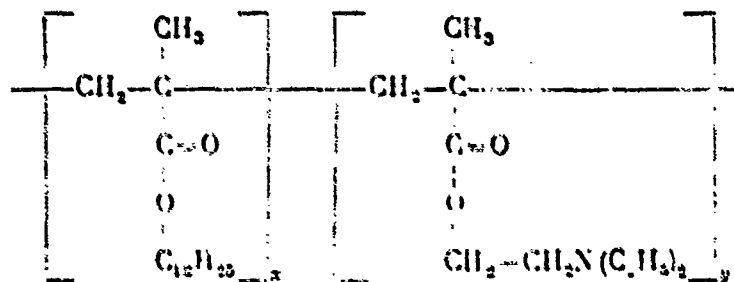


Table 13 lists the multipurpose diesel-oil additive produced by domestic industry, as well as certain experimental versions.

While in 1958 the oils produced with multipurpose additives did not exceed 36% of the total motor-oil production, at the present time, it amounts to at least 50%, and by 1965 nearly all motor oils will be produced with additives for various purposes.

Table 19 gives the basic characteristics of commercial additives in accordance with data from state standards for current technical specifications.

Some characteristics of foreign oils with additives and characteristics of the additives themselves are given in Tables 20 and 21.

TABLE 18. Most Important Commercial and Experimental Multipurpose Diesel-Oil Additives

Наименование (шифр) 1 присадки	Основная характери- стика 2	Отметка о промышлен- ном выпуске присадки 3
4 АЗНИИ-4	5 Сульфонатная при- скадка	6 ТУ 347-53 (снята с производства)
7 АЗНИИ-ЦИАТИМ-1	8 Алкилфенольная при- скадка с высокими анти- коррозионными свой- ствами. Предназначена для дизелей, работаю- щих на малосернистых топливах	9 Выпускается про- мышленностью по ГОСТ 7189-54
10 АЗНИИ-ЦИАТИМ-1ф	11 Отличается от присад- ки АЗНИИ-ЦИАТИМ-1 меньшим содержанием серы. Предназначена для дизелей М-50ф, ра- ботающих на малосер- нистых топливах	12 То же, по ВТУ 371-54
13 ЦИАТИМ-339	14 Присадка, предназна- ченная для дизелей, работающих на топли- вах с содержанием серы до 1,0%	15 То же, по ГОСТ 8312-57
14 АЗНИИ-7	16 То же	—
17 ВНИИ НП 360	18 Смесь алкилфенольной и фосфорорганической присадок	19 То же, по ВТУ НП 31-59
20 ВНИИ НП-22	16 То же	21 То же, по ВТУ НП 33-59

TABLE 18 (Continued)

22 ПМС-19, ПМСЯ СВ-3 НГ-102	23 Сульфонатные присад- ки с высокими моющи- ми свойствами	24 Опытные партии
25 НГ-102у ВНИИ НП-362	26 Смеси сульфонатных с алкилфенольными при- садками	27 Опытные образцы

1) Designation (number) of additive; 2) basic characteristics; 3) comments on commercial production of additives; 4) AzNII-4; 5) sulfonate additive; 6) TU 347-53 (removed from production); 7) AzNII-TsIATIM-1; 8) alkylphenol additive with good anticorrosion properties. Designed for diesels running on low-sulfur fuel; 9) produced by industry in accordance with GOST 7189-54; 10) AzNII-TsIATIM-1f; 11) differs from AzNII-TsIATIM-1 additive in lower sulfur content. Designed for M-50 diesel engines, running on low-sulfur fuel; 12) the same, in accordance with VTU 371-54; 13) TsIATIM-339; 14) additive designed for diesels running on fuels containing up to 1.0% sulfur; 15) the same, in accordance with GOST 8312-57; 16) the same; 17) VNII NP 360; 18) mixture of alkylphenol and organophosphorus additives; 19) the same, in accordance with VTU NP 31-59; 20) MNI IP-22; 21) the same, in accordance with VTU NP 32-59; 22) PMS-19, PMSYa, SB-3, NG-102; 23) sulfonate additives with good detergent properties; 24) experimental batches; 25) NG-102u, VNII NP-362; 26) mixtures of sulfonates with alkylphenol additives.

The English "Anglomol" Company produces several oil additives under the name "concentrates." The "concentrate 612" additive has good detergent properties, while concentrates 609 and 1060 improve the anticorrosion properties and the strength of the oil film. When 6.5% of "concentrate 612" additive is introduced into an oil, the resulting oil will correspond in quality to a "series 2" product.

The "Monsanto" Company produces the Santolube, Santopure and Santodex additives, and others, used to improve various oil properties.

Foreign multipurpose additives of the Paranox type are widely known.

The composition, properties, and production technology involved

TABLE 19. Basic Characteristics of Multipurpose Additives Produced by Domestic Industry

Показатель 1	АзНИИ-ЦИАТИМ-1 ГОСТ 7189-54 2	ЦИАТИМ-339, ГОСТ 8312-57 3	ВНИИ НП-360, ВТУ НП31-59 4	МНИ ИП-22, ВТУ НП32-59 5
6 Вязкость кинематическая при 100°С, сст . . . . .	32-60	15	13-17	17-20
7 Зольность, % . . . . .	4,0-5,5	8,5	13,5-16,0	10
8 Барий, %, не менее . . . . .	2,0	4,7	7,8-9	4
9 Сера, % . . . . .	3,0-4,5	4,0-5,5	1,4-2,0	5-6
10 Фосфор, % . . . . .	—	—	0,8-1,0	1,7
11 Цинк, % . . . . .	—	—	0,7-0,90	—
12 Водорастворимые кислоты и щелочи . . . . .	15	16	—	—
13 Коррозийность, по Пинкевичу, базового масла МТ-16 с 3% присадки на пластинках из свинца, г/м <sup>2</sup> , не более . . . . .	Отсутствие	Щелочная реакция	—	—
14 Моющие свойства по методу ПЗВ базового масла МТ-16 с 3% присадки в баллах, не более . . . . .	6,0	15,0	—	(С 4,5% присадки) 1,7
				0,1
			17 (С 5% присадки) 0,5-1,0	(С 4,5% присадки) 1,7
				0,5-1,0

1) Characteristic; 2) AzNII-TsiATIM-1, GOST 7189-54; 3) TsiATIM-339, GOST 8312-57; 4) VNII NP-360; VTU NP31-59; 5) MNI IP-22, VTU NP32-59; 6) kinematic viscosity at 100°C, sst; 7) ash, %; 8) barium, %, no less than; 9) sulfur, %; 10) phosphorus, %; 11) zinc, %; 12) water-soluble acids and alkalis; 13) corrosion, Pinkevich method, MT-16 base oil with 3% additive, lead plates, g/m<sup>2</sup>, no more than; 14) detergent properties, PZV method, MT-16 base oil with 3% additive, arbitrary units, no more than; 15) none; 16) alkali reaction; 17) with 4.5% additive; 18) with 5% additive.

TABLE 20. Some Physicochemical Properties of Foreign Series 2 Oils

1 Свойства	2 Масла серии 2	
	3 Тип А	3 Тип В
4 Консервность, % . . . . .	3,5	2,5
5 Зольность, % . . . . .	2,0	2,1
6 Щелочность, мг KOH на 1 г масла . . . . .	3,3	0,8
7 Содержание, %:		
8 бария . . . . .	1,53	0,51
9 кальция . . . . .	0	0,11
10 серы . . . . .	0,64	0,60
11 фосфора . . . . .	0,11	0

1) Property; 2) series 2 oil; 3) type; 4) carbon residue, %; 5) ash, %; 6) alkalinity, mg KOH per 1 g of oil; 7) content, %, of:; 8) barium; 9) calcium; 10) sulfur; 11) phosphorus.

TABLE 21. Properties of Additives Produced by "Anglomol" Company

1 Показатели	2 Концентраты		
	609	612	1060
3 Удельный вес при 15,6°C . . . . .	1,11	1,09	1,4
4 Вязкость при 98,9°C, сст . . . . .	9,05	26,5	9,05
5 Содержание, %:			
6 бария . . . . .	0,55	12,2	0
7 цинка . . . . .	8,1	1,3	8,3
8 серы . . . . .	16,0	3,5	6,5
9 фосфора . . . . .	7,7	1,7	8,0

1) Characteristic; 2) concentrates; 3) specific gravity at 15.6°C; 4) viscosity at 98.9°C, sst; 5) content, %, of; 6) barium; 7) zinc; 8) sulfur; 9) phosphorus.

in foreign oil additives form the subject matter for a manifold patent literature [13].

#### OPERATING MECHANISM OF MULTIPURPOSE OIL ADDITIVES

The protective mechanisms of anticorrosion additives and antioxidants may differ, depending on the structure and properties of the additive, and basically involve the following:

- a) the formation of a protective film on the metal, which prevents corrosive agents from penetrating;
- b) retardation of the oil-oxidation process and reduction of oxidation products;
- c) neutralization of acid oil-oxidation products and fuel combustion products.

The various sulfur and organophosphorus compounds have the greatest tendency to form strong protective films on lead and its alloys.

As we have already mentioned, oils made from high-sulfur crudes are less corrosive than oils from low-sulfur crudes. Have the sulfur compounds in the petroleum act as natural additives that form a protective sulfide film on the metal surface. The anticorrosive action of natural sulfur compounds proves inadequate, however, in comparison

with the effectiveness of sulfur-containing additives such as the AzNII-TsIATIM-1, AzNII-7, etc., additives of the sulfides of barium dialkylphenolates type.

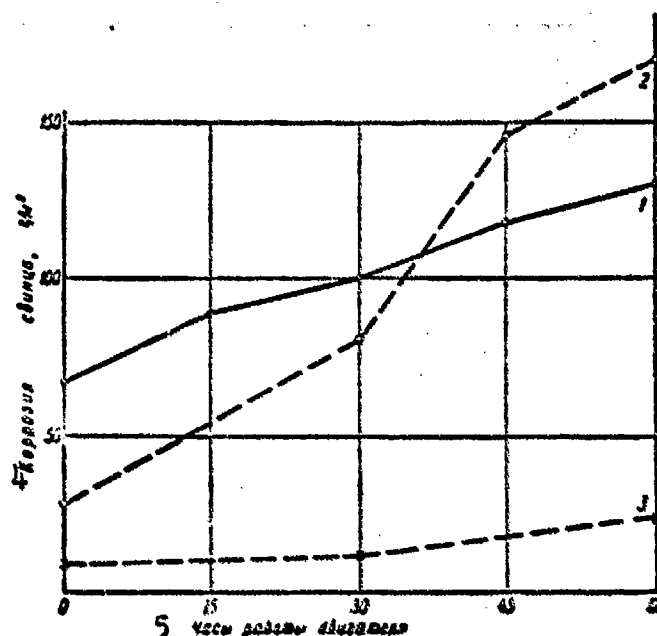


Fig. 10. Effect of additives on corrosiveness of D-11 diesel oil during engine operation. 1) D-11 diesel oil without additives; 2) the same + 3% TsIATIM-339 additive; 3) the same + 3% AzNII-TsIATIM-1 additive; 4) corrosion of lead, g/m<sup>2</sup>; 5) engine operation, hours.

Barium alkylphenolate (APB) is a detergent component included in many complex additives. The sulfur introduced into the APB molecule is extremely active, and reacts with the metal to form a rather strong sulfide film that protects the metal against corrosive reagents, and maintains its integrity during the process of motor operation.

Thus, introduction of sulfur into the APB molecule imparts new properties to it, and makes the additive a multipurpose substance such as the TsIATIM-339, AzNII-7, etc., additives.

The surface of bearing inserts, cast from lead alloys, acquire a characteristic dark-brown color, due to the formation of the protective film, after they have been run with an oil formulated with sul-

fur-containing additives.

Figure 10 shows the effect of additives on the change in corrosiveness of D-11 diesel oil during engine operation.

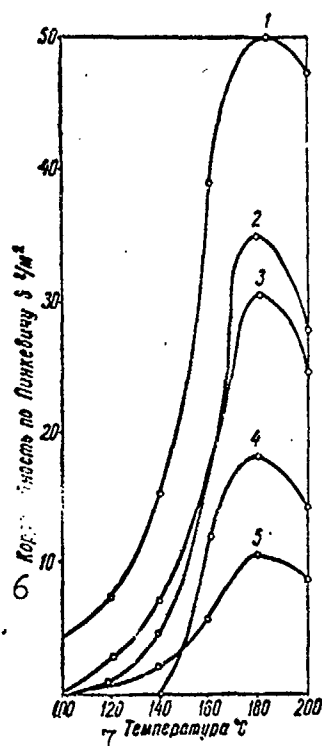


Fig. 11. Corrosiveness of DS-11 oil with various additives as a function of temperature. 1) DS-11 oil with no additive; 2) the same, TsiATIM-339 additive; 3) the same, VNII NP-60 additive; 4) the same, PMS-19 additive; 5) the same, AzNII-7 additive; 6) Pinkevich corrosion,  $\text{g}/\text{m}^2$ ; 7) temperature,  $^{\circ}\text{C}$ .

Oil corrosiveness is determined in a Pinkevich apparatus from the loss in weight of lead strips. As the graph shows, the corrosiveness of oils without additives increases with the length of time that the engine operates.

For oils with the effective AzNII-TsiATIM-1 anticorrosion additive, corrosiveness remained very low over the entire test period.

The TsiATIM-339 alkali additive proved somewhat less effective, which may be due to the lower strength of the protective film and the fact that the additive has less effect on neutralization of acid products, and on the dispersing effect.

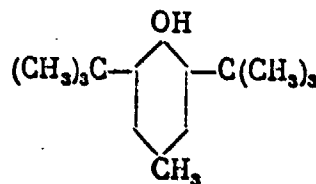
As we know, oil corrosiveness rises with temperature. As Ramayya has shown, a bend in the curve occurs at certain temperatures. This is true of both base oils and oils with additives, and may be explained by the variation in the molecular structure of the oils and additives at the beginning of thermal decomposition. Figure 11, due to V.S. Demchenko, shows the way in which corrosion (by the Pinkevich method) depends on temperature for oils with various additives. It follows from the nature of the curves that the anticorrosion effectiveness of additives does not change in the same way with temperature.



Thus, for example, while at the standard determination temperature of 140°C, an oil with PMS-19 additive has less corrosiveness than with AzNII-7 additive, at higher temperatures, the picture is just the opposite.

Alkylphenols possess antioxidant properties that retard the oxidation rate for hydrocarbon oils.

The best antioxidant properties are shown by the so-called "shielded" phenols, i.e., phenols having alkyl groups attached at the carbon atoms of the benzene ring [20]. The "shielded" phenols include the well-known antioxidant Ionol (2,6-dibutyl-4-methylphenol), which has the structure



The organophosphorus compounds contain as antioxidant components (VNII NP-353, AN-22) in the multipurpose VNII NP-360, MNI IP-22, etc., additives are good antioxidants. The antioxidants also include various amines and their derivatives [50].

Sulfonates have somewhat poorer antioxidant properties, and thus it is recommended that organophosphorus components be introduced into sulfonate additives as antioxidants.

Several investigators [17, 56] have shown that there is a direct connection between the ability of alkali additives to decrease corrosive wear and their ability to prevent the formation of deposits on engine parts. This is explained by the fact that the ashes that form on oil oxidation and fuel combustion not only cause corrosion, but also either act as the basic products that form deposits, or else help to increase the amount and strength of these deposits.

Thus, the alkali properties of additives play a large role in decreasing corrosive wear and the amount of varnish and carbon deposits, especially where sulfur-bearing fuels are used.

Figure 12 gives some results from an investigation into the effect of additive concentration on wear rate, carried out by Yu.S. Zaslavskiy, G.I. Shor, and V.N. Monastyrskiy [17], using an apparatus with radioactive rubbing parts.

In these experiments, vapors of acetic or sulfuric acid were applied to the friction surfaces. As a result, the rate of wear, checked by means of the radioactivity of the oil under study, rose sharply.

Depending on the amount of additive introduced, more or less long-term retardation of the wear rate was observed, followed by a sharp rise, commencing after the alkali additive had been used, in neutralizing the acid.

The neutralizing action of alkylphenols is greater than that of the corresponding sulfates, which is explained by the weak bond of the metal in the alkylphenol molecule, and its tendency to dissociate in the presence of acids.

An oil with an additive retains its alkali properties until all of the additive's alkali component has been used up in neutralizing the acids formed. Thus, the ability of an oil to retain the alkali re-

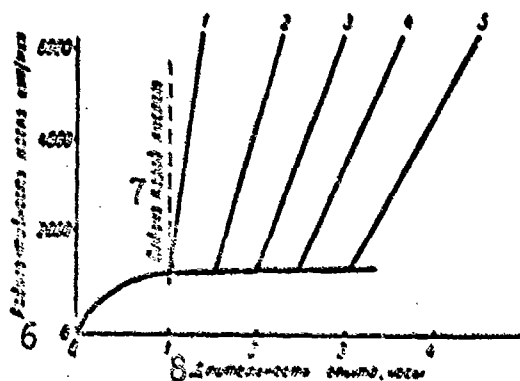


Fig. 12. Effect of neutralizing-additive concentration on the effectiveness with which corrosive wear is retarded. 1) AS-9.5 oil, no ad-

ditive; 2) the same + 1.5% sodium disulfide alkylphenolate; 3) the same + 3% of the same additive; 4) the same + 6% of the same additive; 5) the same + 9% of the same additive; 6) radioactivity of oil, counts per min; 7) application of acid vapors; 8) duration of experiment, hours.

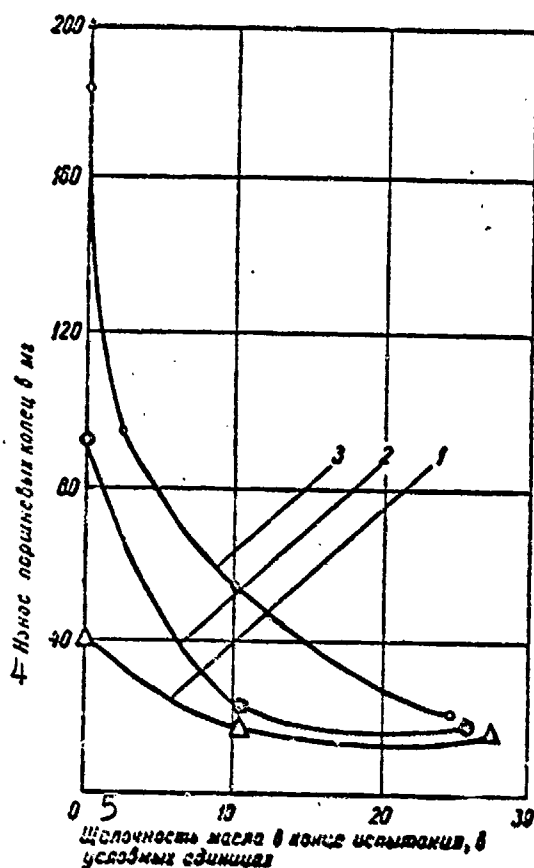


Fig. 13. Wear on piston ring as function of oil alkalinity at end of test, engine operating on fuels with various sulfur contents. 1) Content  $S = 0.2\%$ ; 2) the same,  $S = 1.0\%$ ; 3) the same,  $S = 2.0\%$ ; 4) piston-ring wear, mg; 5) acid alkalinity at end of test, arbitrary units.

action decreases wear and reduces the amount of deposits on the piston, and this is especially evident when an engine is operated on a fuel with a high sulfur content.

Figure 13 shows the results obtained by Kendall [52]; he studied piston-ring wear in a Gardner engine operating on fuels with various sulfur contents and oils with various alkali-additive concentrations.

As we can see from the nature of the curves, high alkalinity has very little effect on wear reduction when an engine uses a low-sulfur fuel, but it is extremely effective where the fuel sulfur content is 1.0 and 2.0%.

Hoyningen-Huen and others [56] have also indicated that there is no relationship between oil alkalinity and wear and piston fouling when a low-sulfur fuel is used.

Mechanism of detergent-additive action. We should first note that the mechanism by which a detergent additive acts has not been studied sufficiently, and the available experimental material only permits certain assumptions as to the essence of this process.

Denison and Kavan [11], and other investigators [59] have used an electron microscope to study the change in oil structure occurring during engine operation; they found that fresh oil represents a highly dispersed system in which very fine insoluble particles of tarry products form and consolidate with increasing length of engine operation. These particles are converted into larger aggregates (micelles), owing to the confluence of fine particles. This is the way in which carbon particles form; these particles, adhering to engine parts, lead to fouling. Figure 14 shows electron microphotographs of used oil with various periods of engine operation.

The purpose of a detergent additive is to prevent the consolidation of carbon particles and the formation of deposits, keeping the particles in the finely-dispersed state, suspended in the oil.

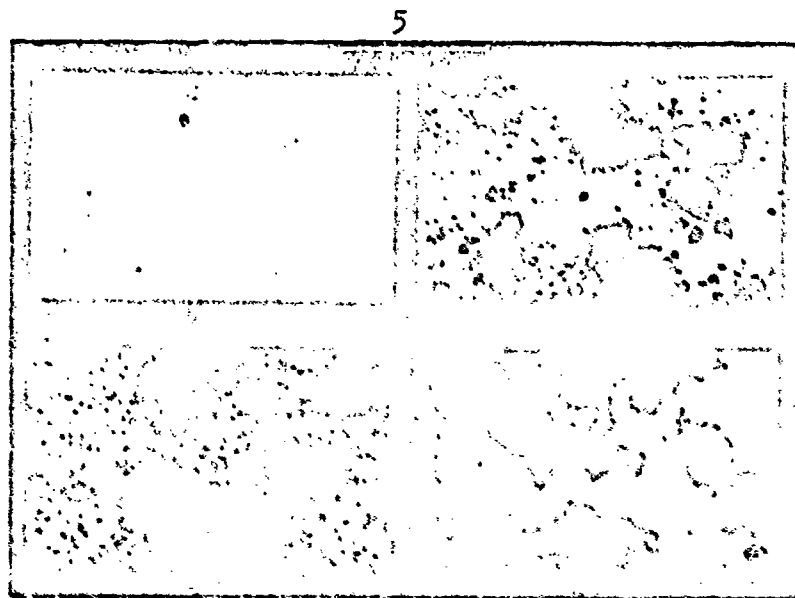


Fig. 14. Variation in carbon-particle size in oil during process of engine operation. 1) Fresh oil; 2) oil after 5 hours of engine operation; 3) the same, after 15 hours; 4) the same, after 40 hours; 5) 1 micron.

An oil with an additive does not represent a true solution, but rather a certain colloidal system in which the additive is dispersed in the form of micelles containing a large number of molecules.

The additive, which is a polar-active substance, is easily adsorbed both on the surface of the metal and on the insoluble oxidation-product particles dispersed in the oil. In this case, the additive par-

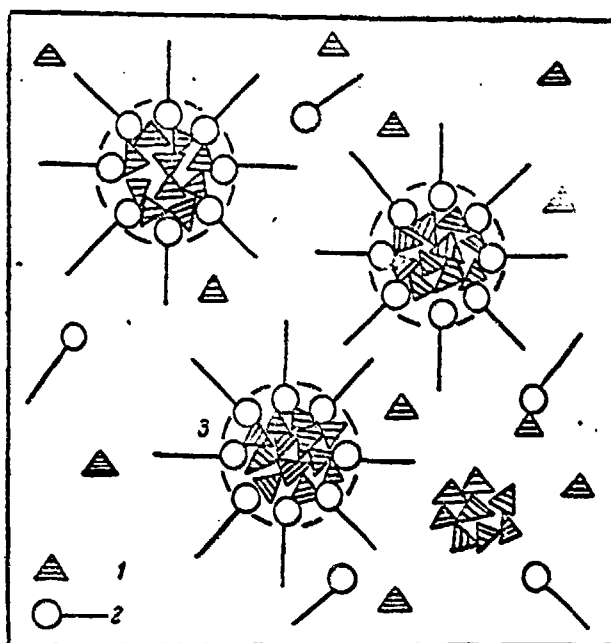


Fig. 15. Dispersing action of detergent additives. 1) Molecule of gum-forming compound; 2) molecule of detergent additive; 3) micelle consisting of gum-forming-compound molecules surrounded by molecules of detergent additive.

ticles surround the consolidating micelles of carbon, preventing them from getting larger and entering the engine parts. Thus, the dispersed carbon particles remain in the oil and are gradually removed from it when the oil passes through oil filters or centrifuges.

Figure 15 shows a conventional diagram illustrating the dispersing effect of a detergent additive.

This representation of the detergent-additive mechanism makes it understandable that there must be some elimination of part of the additive due both to adsorption by metal surfaces and to elimination of the additive together with carbon by the oil filters.

Observations have shown that the greatest rate of engine deposit

formation coincides with the period in which most of the additive has been eliminated and carbon particles are consolidating in the oil.

It should be noted that the effectiveness of additives depends to some degree on the chemical composition of the base oil. According to data of A.V. Druzhinina [13] the naphthene-paraffin hydrocarbons are most sensitive to the action of additives.

#### VISCOSITY ADDITIVES AND DEPRESSANTS

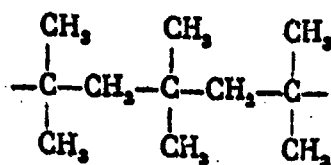
Low-viscosity oils have a flatter curve for the viscosity-temperature relationship. If a low-viscosity liquid contains a dissolved substance whose molecular weight is considerably greater than the molecular weight of the solvent, the viscosity will be raised and at the same time the flatness of the viscosity-temperature curve will be retained.

Thus, various high-molecular-weight products of hydrocarbon polymerization may be used as additives in order to obtain thickened oils.

It should be noted that viscosity additives do not in themselves improve the flatness of the viscosity-temperature curve, whose nature is determined completely by the base oil. Utilization of viscosity additives, however, makes it possible to obtain thick oils whose viscosity-temperature properties are very nearly the same as those of the base oil, and the viscosity of such oils at low temperatures will be considerably below that of ordinary oils having equal viscosity at 100°C.

In 1939, S.S. Nametkin and M.G. Rudenko obtained an additive, which they called Superol.

Superol is a polyisobutylene with a molecular weight of 24,000, i.e., the isobutylene polymerization product has the structure



Another polymer additive is Vinipol, obtained by M.F. Shostakovskiy by polymerization of vinyl-n-butyl ether.

A well-known foreign additive is Paraton(e), which is a solution of pure polyisobutylene (with molecular weight of 30,000) in oil.

Recently, methacrylate viscosity additives have become common; they take the form of polymers of methacrylic acid esters and high-molecular-weight alcohols. In the United States, 50% of all viscosity additives are made up of methacrylic and acrylic esters [28].

Certain polymethacrylates, also called acryloids in the foreign literature, are used to thicken oils, and also are able to lower the oil pour point, i.e., they are depressants.

Other additives that improve viscosity properties and reduce the pour point are the voltolized oils (voltols), which are obtained when an electrical glow discharge acts on an oil.

It is assumed that during voltolization, the high-frequency alternating current causes polymerization processes to occur, and the high-molecular-weight products obtained change the viscosity properties of an oil upon addition. Voltols also improve the oiliness and oxidation stability, but do not improve the anticorrosion or detergent properties of an oil.

The thickening effect produced by an additive consisting of high-molecular-weight compounds depends on the concentration of the additive, the molecular weight of the polymer, and on the properties of the base-oil - the solvent.

It has been established in practice that a molecular weight of 15,000-30,000 is optimum for the polymers used as viscosity additives.

TABLE 22. Viscosity-Temperature Properties of "Avtol" Motor Oils (from Data of Ye.G. Semen-ido)

1 Температура, °C	2 Вязкость кинематическая, сст		
	AK-10	3 AC-5	4 AKЗп-10
150	3,5	2,5	4,1
125	5,5	3,7	6,0
100	10,4	7,1	10,0
50	72	48	45,0
0	5625	2050	1091
-5	11358	3600	1748
-10	—	7049	2886
-20	—	33800	20498

1) Temperature, °C; 2) kinematic viscosity, sst; 3) AS-5; 4) AKZp-10.

Polymers with molecular weights greater than 30,000 do not have adequate thermal or mechanical stability, and find almost no application as motor-oil additives.

Thickened oils. Thickened oils, which have a flat viscosity-temperature curve, have been created as a result of the need for an oil that retains sufficient mobility to ensure easy engine starting at low temperatures while having sufficiently high viscosity in positive-temperature regions.

Examples of such oils are "Avtol" motor oils AKZp-6 and AKZp-10 (GOST 1862-57), thickened with polyisobutylene of molecular weight 15,000-25,000, and MT-14p oil (see Fig. 3).

Petroleum distillates with viscosities at 100°C not exceeding 4 sst are used as the low-viscosity bases for thickened oils; they have a restricted fractional composition. According to data of Ye.G. Semenido [41], a base for thickened diesel oils should contain no more than 5% of fractions distilling at 320°, which, in practice, eliminates the possibility of oil evaporation in the engine circulating system.

It is clear from Table 22 that AKZp-10 thickened oil corresponds



in viscosity at  $100^{\circ}\text{C}$  to summer AK-10 motor oil, while at  $0^{\circ}$ , it has a viscosity that is considerably less than ordinary AS-5 winter oil.

In other countries, thickened oils are called all-purpose (multi-grad) or all-weather oils, and they are assigned a double number in the SAE classification.

Thus, for example, SAE-10W/30 all-weather oil corresponds to SAE-10W winter oil in its low-temperature viscosity, while its viscosity at  $100^{\circ}\text{C}$  lies in the range corresponding to SAE-30 oil.

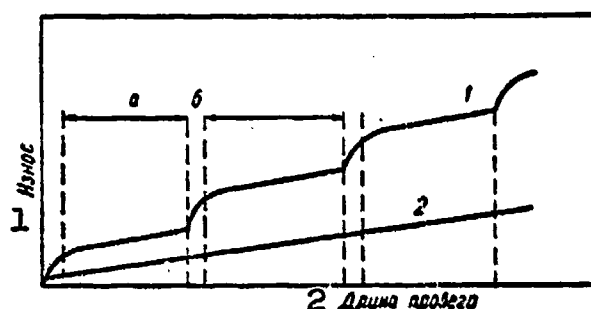


Fig. 16. Nature of piston-ring wear in automobile engine lubricated with ordinary (1) and thickened (2) oils. a) Road-test wear; b) starting wear. 1) Wear; 2) length of run.

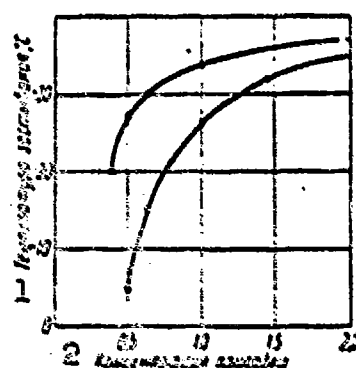


Fig. 17. Effect of AzAIP depressant on pour point of AK-6 oils obtained from various crudes. 1) Pour point,  $^{\circ}\text{C}$ ; 2) additive concentration.

The advantages of thickened oils lie primarily in the improvement of starting characteristics. Utilization of MT-14p thickened oil makes it possible to start a cold diesel engine (provided the fuel in the cylinders ignites) to temperatures of  $-32^{\circ}$ .

Motor tests with a GAZ-51 automotive engine, carried out by N.G. Puchkov [35] at low temperatures yielded the following limiting temperatures at which it is possible to turn the engine over with the starter in order to

start the engine when various oils are used:

Avtol 6, distillate .....	-16, -17°
Avtol 4, distillate .....	-21, -22°
Avtol 6, thickened .....	-24, -25°
Avtol 4, thickened .....	-28, -30°

As we know, the wear on rubbing parts is greatest when a cold engine is started and the oil supply is inadequate owing to the high viscosity of the oil at low temperatures.

Thickened oils, which have a considerable lower viscosity at low temperatures, provide a better supply of oil to all rubbing parts during starting of an engine, and result in less wear.

Figure 16 shows the results of continuous observations of the rate of wear of piston rings in an automobile engine; the tests were carried out by English investigators using a radioactive-isotope method [58].

When Type SAE-10W thickened oil is used, there is a uniform increase in wear, while with operation on ordinary oil, a sudden increase in engine wear is noticed when it is started after standing overnight.

In addition, thickened oils with low-viscosity base oils result in lower engine friction losses than is the case with ordinary oils, and thus offer some advantage in extra power and fuel savings.

Additives reducing the oil pour point (depressants). A very common additive of this group is the AzNII (GOST 8443-57) depressant, synthesized by A.M. Kulihev, O.A. Geyman, and S.Kh. Shkiyan. The additive is a product of the condensation of naphthalene with a chlorinated paraffin and according to the technical specifications from the standard mentioned, the addition of 0.1% of AzNII depressant to AK-15 oil reduces the pour point by at least 10°C.

The magnitude of the reduction depends greatly on the chemical

composition of the oils. Type AzNII depressant is most effective in reducing the pour point of low-paraffin oils. As Fig. 17, due to N. V. Brusyantsev [5], shows, the greatest reduction in oil pour point is caused by the first batches of depressant. A further increase in additive concentration above 1.0-1.5% is relatively ineffective. As a rule, AzNII depressant is normally added to commercial diesel oils and to avtols in concentrations not exceeding 0.5%.

The multipurpose AzNII-TsIATIM-1 (GOST 7189-54) additive is also used as a depressant; in addition, it has good anticorrosion and, to some degree, detergent properties.

Table 23 gives data on the effect of various depressants on oil pour points [28].

Other additives. In addition to the anticorrosion, detergent, viscosity, and pour-point depressant additives discussed above, there are several other types of additives which, however, are used primarily not for diesel oils, but for oils intended for other types of engines and mechanisms. Thus, we shall only give brief mention to these additives.

Antiseizing additives or additives improving the lubricating properties of oils. These additives increase the oiliness and reduce the coefficient of friction for a mechanism. This type of additive is normally introduced into transmission oils designed for the lubrication of rubbing surfaces in mechanisms with high unit pressures, for example, for hypoid gears. These additives include chlorinated hydrocarbons, xanthates, and various sulfurized products. In other countries, oils for extreme pressures are called EP oils (extra-pressure oils).

Antiform additives are designed to break up water-oil emulsions that form in the oil system when the oil spatters in the engine crank-

case. This type of additive includes certain organosilicon compounds known as polysiloxane fluids (PMS-200 additive).

TABLE 23. Pour Point of Turbine Oil Produced from Eastern Crudes, Various Additives (Data Due to L.A. Potolovskiy)

1 Присадка	2 Температура застывания, °C				
	3 Исходное масло без присадки	4 После добавления присадки, %			
		0,10	0,25	0,50	1,0
5 Депрессатор АзНИИ	-10	—	—	-17	-18
6 АзНИИ-ЦИАТИМ-1	-10	—	-20	-25	-29
7 Акрилоид 150 (импортный)	-10	—	-23	-28	-28
8 Полиметакрилат, М-15600	-10	-23	-33	-37	-40

1) Additive; 2) pour point, °C; 3) initial oil, no additive; 4) after introduction of additive, %; 5) AzNII depressant; 6) AzNII-TsIATIM-1; 7) Acryloid 150 (imported); 8) polymethacrylate, M-15,600.

### Chapter 3

#### TEST METHODS FOR OILS AND ADDITIVES

##### EVALUATION OF OILS WITH LABORATORY APPARATUS

In order to evaluate the suitability of an oil or additive for utilization under actual operation conditions, it is necessary to have available reliable test methods. The preliminary evaluation of oil and additive quality is carried out with laboratory apparatus, while the final decision as to whether or not a given oil is suitable for a particular engine can be made only after extensive motor tests have been carried out.

Additives are introduced into a base oil in order to improve its operating properties. However, the results of a determination of the ordinary physicochemical characteristics of an oil with an additive such as the ash content, carbon residue, acidity, etc., will normally give no basis for a judgment as to the improvement in oil quality. The introduction of 3-5% of an alkylphenol additive increases the ash content and carbon residue, causes the oil to display an alkali reaction, and at first glance appears to impair the oil characteristics; in order to evaluate oil operating properties, therefore, the motor-oil standards specify several additional indicators characterizing corrosiveness, detergency, and thermal-oxidation stability; these characteristics are to be determined with laboratory apparatus.

Among the most common methods for determining the corrosiveness of an oil are determinations of corrosiveness with the apparatus of V.S. Pinkevich and EX-2 apparatus, developed by K. S. Ramayya (State

All-Union "Order of Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute) (NAMI).

The PZV method is a very reliable way of determining oil dete - gency. The standards for oils with additives also specify an evaluation of thermal-oxidation stability.

Well-known methods exist for determining the motor volatility of oils (K.K. Papok), the tendency of oils to form varnish, using apparatus to K.S. Kyuregyan, oil oxidizability, in a DK-2 instrument, and other test methods for oil operating properties using laboratory apparatus.

Determining oil corrosiveness by the Pinkevich method (GOST 5162-49). The method consists in evaluating oil corrosiveness from the change in weight of a metal strip that is subjected alternately to immersion in the tested and raising to the air; the test is carried out in a Pinkevich apparatus for 50 hours at an oil temperature of 140°C.

Figure 18 gives a diagram of a Pinkevich apparatus.

As a rule, lead strips are used to evaluate oil corrosiveness; for research purposes, however, plates of lead-bronze or other bearing alloys may be used. Oil corrosiveness is expressed by the change in weight of the strip per unit area.

The red-plate corrosiveness of fresh oils without additives ranges from 10 to 100 g/m<sup>2</sup>, while for oils with additives, it does not exceed 10-12 g/m<sup>2</sup>. Where lead-bronze plates are used, the change in weight is one-third to one-fourth that found with red plates.

In determining the corrosiveness of oils containing effective anticorrosion additives, an increase in strip weight is sometimes obtained owing to the appearance of a protective film that forms when the metal reacts with the elements of the additive. The Pinkevich me-

thod has been used for several years, and it gives completely reliable results; recently, however, the method has begun to give way to the faster corrosion-determination method using the DK-2 apparatus.

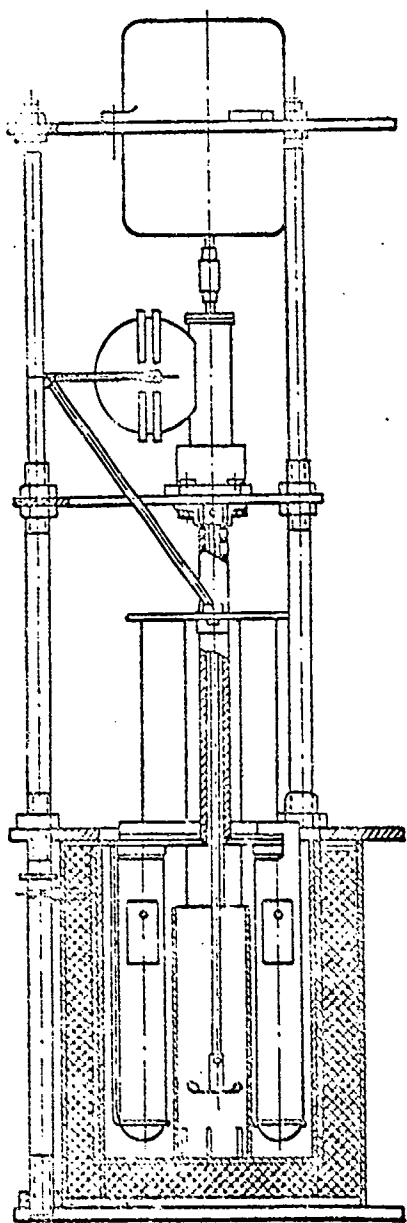


Fig. 18. Diagram of Pinkevich apparatus for determining oil corrosiveness.

The method described gives corrosiveness values that are close to those obtained with the Pinkevich apparatus, and has the advantage of requiring a shorter determination period.

Recently, a method proposed by the NAMI for determining oil oxi-

#### Determining oil corrosiveness by

K.S. Ramayya's method. The method of determining oil corrosiveness with a DK-2 apparatus of the NAMI (GOST 8245-56) proposed by K.S. Ramayya [39] is also based on a determination of the weight lost by a lead strip subjected periodically to the action of the tested oil and air, both heated to  $140^{\circ}\text{C}$ , for a 10-hour period.

Figure 19 shows a DK-2 apparatus.

The lead strip 5, located in the specially-shaped flask 4, is alternately immersed in the oil and subjected to the action of the air as the flask is rotated about the axis of the instrument by means of the electric motor 1 and reducing gear 2.

The temperature is held constant by means of the oil bath 3, which is provided with a mixer 6, electric heater, and temperature control.

·dation has come into common use. The oil is oxidized in the DK-2 apparatus of the NAMI at a temperature of  $200^{\circ}\text{C}$  for 50 hours; the degree of oxidation is judged primarily from the accumulation of insoluble sediment due to oxidation products, as well as from the increase in viscosity [36]. Oils with high oxidation stability yield minimum amounts of sediment.

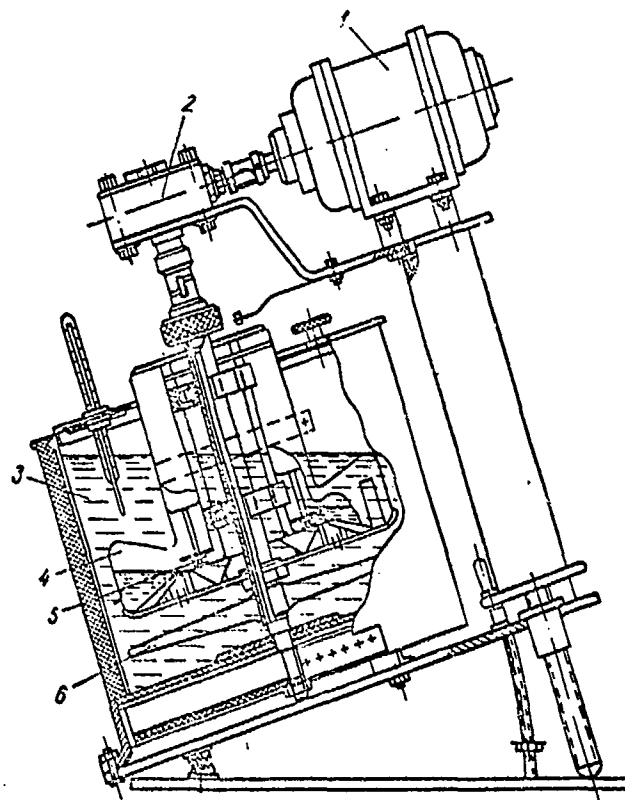


Fig. 19. Diagram of NAMI DK-2 apparatus for determining oil corrosiveness.

Determining detergency by the PZV method (GOST 5726-53). This method, developed by K.K. Papok, A.P. Zarubin, and A.B. Vipper is based on a brief test of the oil in a special PZV apparatus, followed by evaluation of piston fouling on an arbitrary scale.

The PZV apparatus takes the form of a single-cylinder motor (cylinder diameter 52 mm, piston stroke 52 mm), driven by an electric motor. The cylinder head and walls are heated by electric heaters. Figure 20 shows a diagram of the PZV apparatus.



The following operating conditions are maintained during tests:

Speed .....	2500 rpm
Cylinder-head temperature .....	300°C
Center of cylinder temperature .....	225°C
Oil in crankcase temperature .....	125°C
Induction air temperature .....	220°C
Quantity of oil tested .....	250 ml
Length of test .....	2 hours

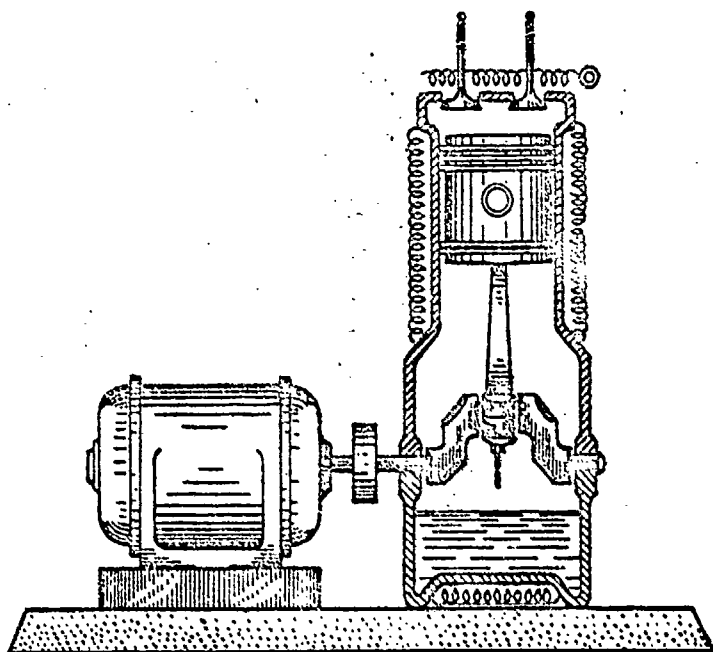


Fig. 20. Diagram of PZV apparatus.

At the conclusion of the test, the piston is inspected, and an estimate made as to the quantity and color of the varnish deposits on the side surface of the piston; the estimate is made by comparing it with a standard color scale, reproduced in Fig. 21.

A completely clean piston with no varnish deposits receives the highest rating - 0. If the entire side wall of the piston is covered with black varnish, the lowest rating - - is given.

Varnish-formation determinations by the PZV method agree well with results obtained by motor tests in an engine [36].

The thermal-oxidation stability of oils (GOST 4953-49), determined by the method of K.K. Papok, is expressed in terms of the time (in minutes) required to convert an oil under the given test conditions into a varnish film.

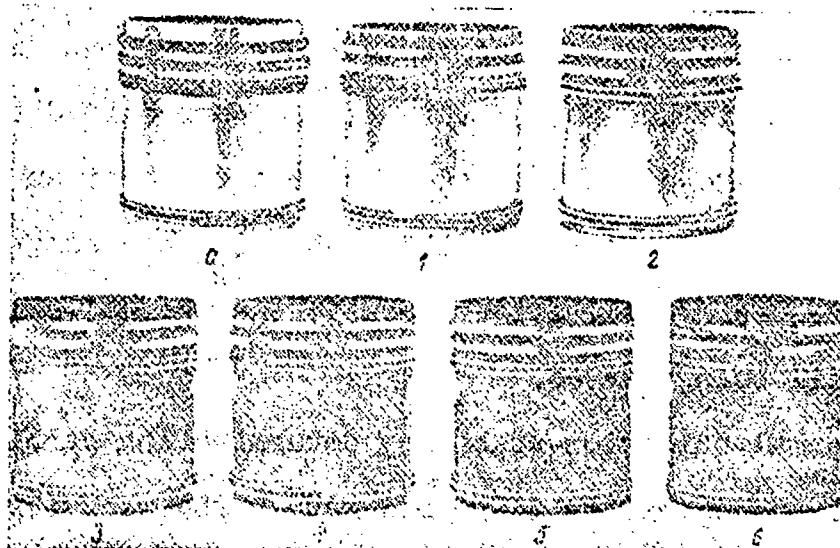


Fig. 21. Scale used to evaluate varnish formation on pistons of PZV apparatus (0 represents the best possible rating with respect to piston fouling).

TABLE 24. Effect of Additives on Oxidation of MT-16 Oil

1 Масло и присадка	2 И/Л при 250° C за 30 мин, %	3 Термоокислительная стабильность по методу Папок при 250° C в минутах
4 Масло MT-16 без присадки	67/18	18
То же + 3% НГ-102у 5	62/16	19
• + 3% СБ-3 6	64/5	18
• + 3% ДФ-1 7	56/0	51
• + 3% ВНИИ НП-353 8	53/0	63
• + 6.5% СБ-3 + 3.5% АН-22 9	52/0	80

1) Oil and additive; 2) I/L at 250°C, 30 min, %; 3) thermal-oxidation stability, Papok method, 250°C, minutes; 4) MT-16 oil. no additive; 5) the same, + 3% NG-102u; 6) the same + 3% SB-3; 7) the same + 3% DF-1; 8) the same + 3% VNIИ NP-353; 9) the same + 6.5% SB-3 + 3.5% AN-22.

Thermal-oxidation stability is determined by means of a special varnish-forming device, in which the required temperature (usually 250°C) is maintained.

The oil is poured within metal rings located on a steel disk, which is placed into the varnish-forming device; the disk is left there until the oil has been converted into a varnish film. A lever-type dynamometer is used to measure the force required to remove the burnt ring from the disk. The time required for a given temperature to convert the oil into a varnish film that holds the ring with a force of 1 kg serves as a qualitative index to the thermal-oxidation stability of the oil being tested.

The thermal-oxidation-stability determination carried out by this method serves to characterize approximately the behavior of the oil in an engine in the piston-ring zone, from the viewpoint of piston-ring burning and the formation of varnish deposits. At 250°C the thermal-oxidation stability determined by the K.K. Papok method normally lies in the 15-25 min range for base oils (no additives). By introducing 3-5% of antioxidants such as dialkyldithiophosphates, the thermal-oxidation stability may be increased to 60-80 min, which is very important in reducing the tendency of an oil to form varnish and cause piston-ring burning.

Motor volatility, working fraction, and varnish (GOST 5737-53).

This method, developed by K.K. Papok and his associates, characterizes oil volatility when it comes into contact with hot surfaces of engine parts, and its tendency to form varnish.

The determination is made in terms of the weight loss of small quantities of oil applied in a thin layer to special metal plates (evaporators), which are placed into the varnish-forming device described above, where they are held at 250°C for 30 min.

The oil weight lost due to distillation of the light fractions, expressed in percent, is an index to motor volatility. The liquid part of the oil, removed by the solvent, is taken as the working fraction of the oil, while the portion remaining undissolved on the evaporator is taken as the varnish.

As a rule, the oil is characterized by the ratio of the motor volatility (I) to the amount of varnish (L) at a given temperature. Thus, for example, for MS-20 oil at 250°C, the ratio is  $I/L = 61/20$ .

Table 24 gives values of  $I/L$  and the thermal-oxidation stability for MT-16 oil with various additives. It is clear from these data that the sulfonate additives (NG-102 and SB-3) which, as we know, have good detergent properties, have little effect on the tendency of an oil to withstand the oxidation process. Phosphorus-containing additives - antioxidants (DF-1, VNII NP-353, AN-22) - on the other hand, change the  $I/L$  ratio considerably, and improve the thermal-oxidation stability.

Thus, in order to obtain an additive that combines good dispersing characteristics, contains sulfonates with high thermal-oxidation stability, we attempt to obtain a mixture of sulfonates with organophosphorus antioxidants. One such experimental blended additive is a mixture of barium sulfonate (SB-3) with the antioxidant AN-22 which, as the table shows, has good thermal-oxidation stability.

The tendency of oils to varnish formation may also be determined with S.K. Kyuregyan's apparatus [26]; an over-all view of this device is shown in Fig. 22.

A steel ring 3 with a polished surface is attached to a plate 4 within which is located an electrical helical heater. Both ring and plate are rotated by an electric motor through a worm gear located within the housing. On the ring, three aluminum supports 2 hold the load disk 1, which is coupled to a spring that keeps it from turning.

A thin layer of the oil to be tested is applied to the ring. When the ring rotates, friction appears between it and the load-disk supports; as a result, the disk turns somewhat, twisting the spring.

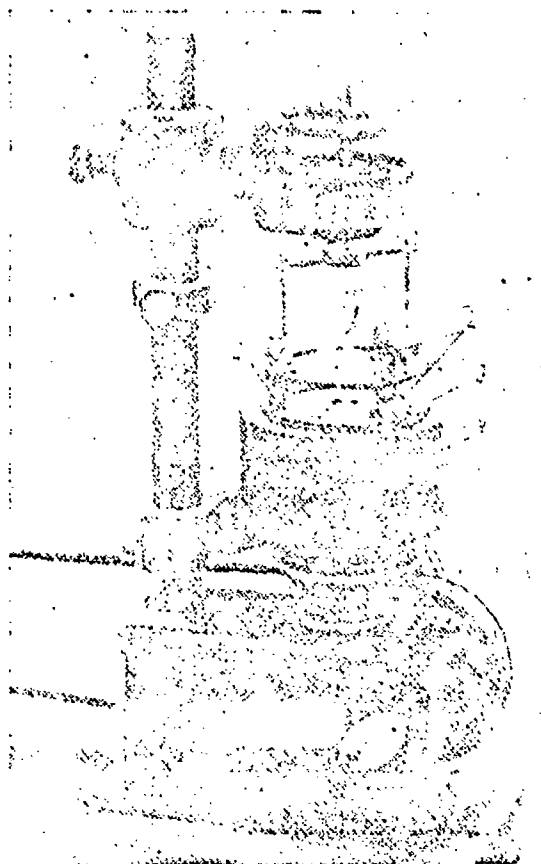


Fig. 22. Kyuregyan device for determining the varnish-forming tendency of oils.

As long as the oil has not changed into varnish, the friction is slight and the angle of rotation of the spring is small. As soon as varnish begins to form, the amount of friction increases sharply and the angle of rotation of the disk increases considerably. The oil quality is determined from the length of time required to form the varnish at 250°C, in minutes.

Table 25 gives the varnish-formation times for a diesel oil with various additives; the tests

TABLE 25. Results of Varnish-Formation Determinations for DS-11 Oil with Various Additives Using Kyuregyan Apparatus

1. Масло и присадки	2. Период лако- образования в минутах
3. Масло ДС-11 без присадки	12
То же + 8% ПМС-19 4	13
• 10% СБ-3 5	16
• 5% БФК-1 6	18
• 3% ТСИАТИМ-339 7	23
• 3% АЗНИИ-7 8	25
• 6% ВНИИ ИИ-330 9	38
• 6% МНИИ ИИ-2210	42
Масло «Мобилгард» (импортное) 11	56

1) Oil and additive; 2) varnish-formation period, minutes; 3) DS-11 oil, no additives; 4) the same, + 8% PMS-19; 5) the same, + 10% SB-3; 6) the same, + 5% BFK-1; 7) the same, + 3% TsiATIM-339; 8) the same, + 3% AzNII-7; 9)

the same, + 6% VNII NP-360; 10) the same, + 6% MNI IP-22; 11) Mobil-guard (imported) oil.

were carried out at the Central Diesel Scientific Research Institute. It follows from these data, as from the data of Table 24, that sulfonate dispersing additives (PMS-19, SB-3) do less to decrease the tendency toward varnish formation than alkylphenol and phosphorus-containing additives of the VNII NP-360 type.

#### OIL MOTOR TESTS

Testing oils and additives in single-cylinder engines. At present, there is no one single standard method in the Soviet Union for conducting motor tests on oils, although work is being carried out in this direction.

The most common methods for determining oil quality use the special UIM-NATI apparatus and the Type IT9 apparatus.

The oil-testing apparatus (UIM) developed by the NATI [49] represents a single-cylinder section of the D-54 (Ch 12.5/15.2) trapdoor diesel engine, mounted on a universal crankcase. The universal crankcase makes it possible, where necessary, to change to a cylinder-piston system of different size. Thus, for example, in one version of this apparatus (the UIM-2 engine) the installed cylinder and piston have the dimensions of those used in the SMD (Ch 11.5/13) combine diesel.

Figure 23 gives an over-all view of the UIM apparatus.

In this test, the cooling fluid is held at a higher temperature than in operating plants; thus, it is possible to determine the tendency of an oil to form carbon and varnish within a relatively short time period.

Table 26 compares basic data characterizing oil test conditions for a UIM-NATI device and other apparatus used to determine oil qual-

ity.

TABLE 26. Methods of Determining Oil Quality with Single-Cylinder Apparatus

1 Наименование методики	2НATI	3ВНИИ НП	4ГСМ-20
5 Двигатель . . . . .	14 УИМ-НАТИ	15 ИТ9-3	ИТ9-5
6 Число оборотов двигателя . . . . .	1300	1200	1200
7 Топливо . . . . .	16 Дизельное	17 Бензин	
8 Расход топлива, кг/час . . . . .	2,6	0,98	1,30
9 Продолжительность испытания, час . . . . .	45	10	20
11 Количество испытуемого масла, кг	10-12	2	2
Режим испытания:			
12 а) температура масла, °C . . . . .	100	85	100
б) температура охлаждающей жидкости, °C (этиленгликоль)			
13 Оценочные показатели:	135	1500	220
	18 а) пригорание поршневых колец, количество и характер отложений на поршне б) коррозионность масла, определяемая по потере веса металлических пластин, установленных в картере		

1) Name of method; 2) NATI; 3) VNII NP; 4) GSM-20; 5) motor; 6) motor speed; 7) fuel; 8) fuel flow rate, kg/hr; 9) duration of test, hours; 11) quantity of oil tested, kg; 12) test conditions: a) oil temperature, °C; b) cooling-liquid temperature, °C (ethylene glycol); 13) characteristics evaluated; 14) UIM-NATI; 15) IT9-3; 16) diesel fuel; 17) gasoline; 18) a) burning of piston rings, quantity and nature of deposits on piston; b) corrosiveness of oil as found from loss in weight of metal strips mounted in crankcase.

Table 27 gives test results obtained by the UIM-NATI apparatus [40] for several specimens of domestic and foreign oils, and gives comparative values for thermal-oxidation stability characteristics as determined with a PZV setup.

The Type IT9 apparatus has as its basic function the determination of fuel ignition points (determination of octane and cetane numbers). V.F. Fillippov [47] has suggested that the IT9-3 apparatus be used, following some modification, for oil tests. Here the motor in the IT9-3 apparatus operates at higher speed (1200 rather than 900 rpm, the speed used in determining octane numbers) and with the cooling liquid and the crankcase oil at higher temperatures.

As a result of the increased combustion intensity, after 10 hours of engine operation, it is possible to determine oil quality from the number of burnt rings, and from the amount and nature of deposits on

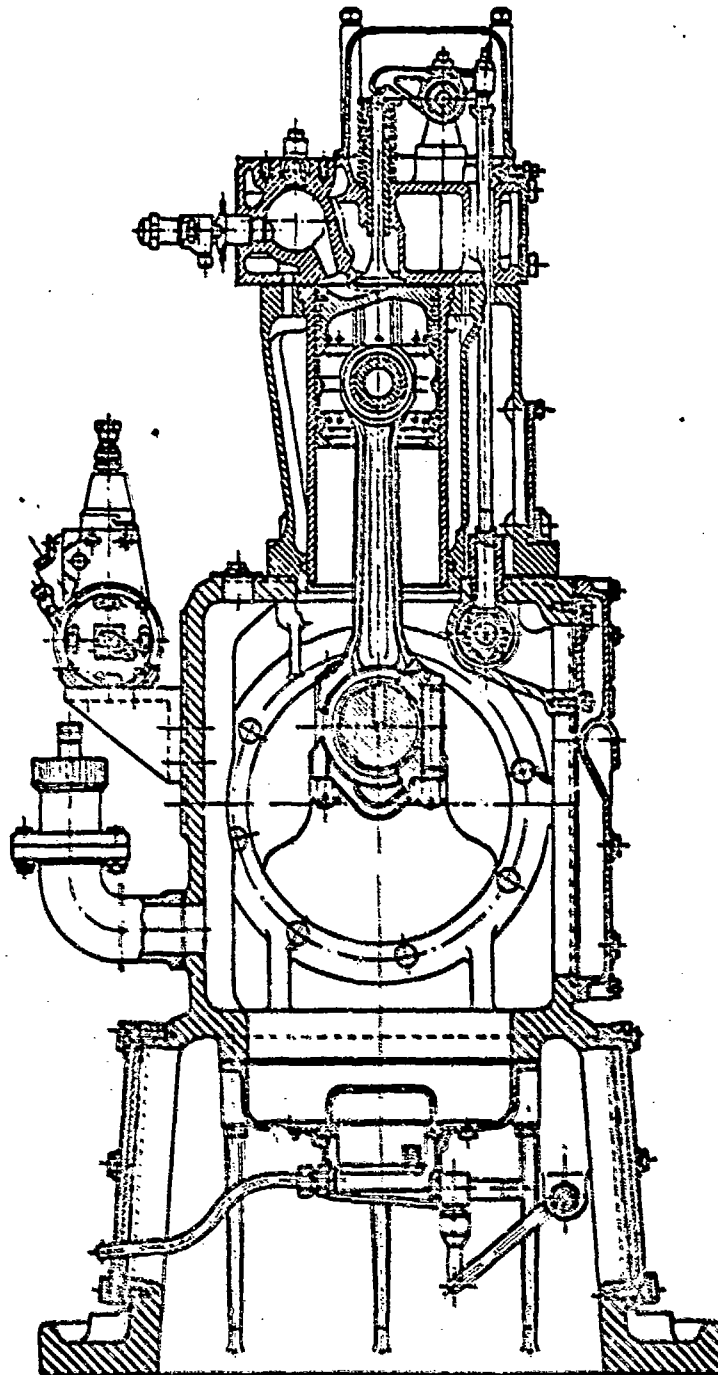


Fig. 23. Diagram of UIN-NATI apparatus.

the piston.

A similar method for evaluating oil quality using a IT9-5 carburetor apparatus, known as the GSM-20 method, was suggested by K.K.



TABLE 27. Comparative Determination of Oil Detergency with UIM-NATI Apparatus and Motorless Devices

1 Масло	2 Моющие свойства по ИЗВ, баллы	3 Термоокис- лительная стабиль- ность при 250°, мин	4 Оценка моющих свойств на УИМ- НАТИ, баллы
Машинное СУ без присадки 5	4.5	20	39
То же + 3% ЦИАТИМ-339 6	2.0	24	15
Дизельное Дп-11 (с присадкой АзНИИ - ЦИАТИМ-1) 7	3.5	20	39
То же (с присадкой ЦИАТИМ-339) 8	3.0	44	19
Импортированное SAE-30 (премиальное) 9	3.5	57	16
Римула Шелл 30 HD 10	0	68	7

1) Oil; 2) detergency, PZV method, arbitrary units; 3) thermal-oxidation stability, 250°, min; 4) determination of detergent properties with UIM-NATI, arbitrary units; 5) SU machine oil, no additives; 6) the same, + 3% TsiATIM-339; 7) Dp-11 diesel oil (with AzNII-TsiATIM-1 additive); 8) the same (with TsiATIM-339 additive); 9) imported SAE-30 (premium); 10) Emba crude.

TABLE 28. Comparative Determinations of Properties of Oils with Additives on IT9-5 Apparatus (GSM-20 Method) and PZV Apparatus

1 Масло, присадка	2 Оценка по методу GSM-20		4 Корро- зия за 10 час, г/м²	5 Моющие свойства по ИЗВ, баллы
	3 Лакообразован- ие, %			
	за 5 час	за 20 час		
ДС-11 без присадки 6	65	—	70	3.5
То же + 4% ЦИАТИМ-339 7	25	45	6	2.0-1.5
То же + 4.5% МНИ ИР-22 8	20	35	7	1.0
МГ-16 (эмбаскред) без присадки 9	100	—	60	—
То же + 3% ЦИАТИМ-339 10	35	70	18	1.5
То же + 3% АзНИИ - ЦИАТИМ-1 11	35	100	1	2.5-3.0
То же + 3% АзНИИ-4 12	100	—	—	3.5
Римула Шелл 30 HD 13	0	5	0	0

1) Oil, additive; 2) determination by GSM-20 method; 3) varnish formation, %; 4) corrosion in 10 hours, g/m²; 5) detergency, PZV method, arbitrary units; 6) DS-11, no additives; 7) the same, + 4% TsiATIM-339; 8) the same, + 4.5% MNI IP-22; 9) MG-16 (Emba crude), no additives; 10) the same, + 3% TsiATIM-339; 11) the same, + 3% AzNII-TsiATIM-1; 12) the same, + 3% AzNII-4; 13) Rimula Shell 30 HD.

Papok, A.P. Zarubin, and G.V. Zakharov [34].

In both of these methods, oil corrosiveness is determined from the weight loss of lead, lead-bronze, or other metal strips installed in the engine crankcase.

Tables 27 and 28 compare the results of oil tests on different apparatus. As these data show, determinations of detergency with UIM-NATI and GSM-20 apparatus agree well with the results obtained on PZV apparatus. The results of oil tests with motorless devices, naturally, do not give a definitive answer to the question of how given oils will behave in service. The results, however, permit tested oils to be classified quite definitely into groups on the basis of relative additive effectiveness:

- a) oils without additives or with the relatively ineffective Az-NII-4 and AzNII-TsIATIM-1 additive;
- b) oils with phosphorus-containing additives (MNI IP-22);
- c) oils with alkylphenol additives of the TsIATIM-339 type;
- d) oils for especially severe service conditions of the Rimula-Shell 30 HD type.

In addition to these special apparatus described, quick tests of oils and additives are frequently made with single-cylinder sections of series-produced small diesels of the tractor type or such motors as the Ch 8.5/11, Ch 10.5/13, D-6, etc. The minimum duration of selection tests for oils and additives in series-produced diesel engines is normally 50-100 hours. Tests of this length permit the determination not only of the tendency of an oil to form carbon, but also yield certain comparative data on engine wear as a function of the oil or additive used.

Since direct micrometer measurement of engine parts in this type of quick test cannot yield reliable data, one of the following methods

must be used to measure wear in this case:

determination of the weight loss of piston rings and bearing liners, and in some cases of other small rubbing parts that are in contact with the oil fuel, by precision weighing of the carefully cleaned parts before and after the test;

the method of cut crescents, which permits determination of cylinder-sleeve and piston-ring wear over a 25- to 100-hour period of engine operation;

determination of the iron contained in the oil and on the filters, which makes it possible to construct a "wear line" and compute the over-all (total) engine wear during the test period;

the radioactive-isotope method.

The method of determining the wear rate by means of radioactive isotopes, which has become very common in recent years, consists in imbedding a plug of a radioactive element, normally cobalt 60, in the cylinder-sleeve wall or in a piston ring, or in using a piston ring that has been made radioactive; as the rubbing elements, including the radioactive plug, wear, radioactive abrasion products accumulate in the oil. Thus, by monitoring the activity of oil samples with a counter, it is possible to judge the degree of engine-part wear in the zone "labeled" by the radioactive element. The radioactive-isotope method permits monitoring primarily of the relative wear, i.e., it yields comparative data on the effect of various types of fuels, oils, and additives on the rate at which engine-parts wear. By carrying out additional experiments, monitoring the iron content of the oil, it is possible to obtain a basis for an approximate calculation of the absolute wear.

An advantage to the radioactive-isotope method is its rapidity, since it permits the relative wear to be determined in the course of

several hours of engine operation.

A drawback to the method is the need for taking several measures to ensure safe working conditions for the attendant personnel.

Bench and operating tests of oils in full-size engines. The first quick tests of oils and additives on single-cylinder apparatus are preliminary in nature, and make it possible to select the best specimens of a series of tested oils or additives for subsequent long-bench testing under conditions similar to operating conditions. The comparison of various oils, fuels, additives, and combinations of additives, selection of optimum additive concentrations, the effect of oil quality on the choice of the most effective additives - all these questions should first be approached by tests on single-cylinder apparatus, since it would be economically undesirable to carry out long-term tests on high-power diesel engines in order to solve such problems. The final evaluation of the suitability of the oil specimens that have been preselected, however, can be made only after tests on a full-size engine.

This type of bench test normally lasts 500-1000 hours under conditions corresponding to actual engine operation, with the wear on basic parts measured by micrometer methods.

As an example, we shall consider the bench-test method used at the Malyshev Plant to select fuels and oils for Type 2D100 locomotive diesel engines [42].

The plant has carried out a long series of tests of fuels with various sulfur contents and of oils with additives, with the aid of ensuring normal engine operation with fuels and oils made from Eastern high-sulfur crudes.

Tests lasted about 600 hours with great care taken to ensure identical test conditions for each specimen of oil additive. As the

basis for comparison, i.e., the standard, measurements of wear, carbon formation, and other indices were taken that characterize the condition of an engine following tests with low-sulfur GOST 4749-49 fuel and D-11 Baku oil with 3% AzNII-7 additive, which were used in the acceptance tests for this engine.

The engine was operated under variable load conditions, with frequent changes from no load to full load, as is characteristic of locomotive-diesel operation.

The following measurements were made in carrying out the factory tests:

- a) measurement of engine power, fuel and oil consumption, measurement of piston temperature, and all operating characteristics;
- b) micrometer determination of wear on cylinder sleeve, crankshaft crankpins, piston pins, bearing linings, and determination (by weight) of wear on piston rings;
- c) determination by weight of carbon deposits on pistons, in ring grooves, scavenging and exhaust ports, as well as deposits on oil filters and centrifuge rotor;
- d) measurement of oil performance indices during the test, including monitoring of the additive content of the oil.

This test program permitted a very complete evaluation of oil operating properties under actual conditions.

The most important results of factory tests of oils with additives, carried out on the 2D100 engine are given in Chapter 4.

This type of extended bench test makes it possible to decide on recommendations for oils for operating tests in several actual applications (locomotives, ships, stationary plants, etc.).

Foreign motor-test methods for lubricating oils. As we have already described in Chapter 1, in other countries motor lubricating oils

are classified by their conditions of application into ordinary oils and oils for heavy and extremely severe duty. The latter group is in turn divided into series 1, 2, and 3, depending on the degree of engine supercharging and operating conditions; the oil grade is determined by the amount and effectiveness of the additives introduced. An oil is classified into a given group or a series on the basis of motor tests carried out by a standard method on special engines.

Quick test methods lasting 36-100 hours are designed for evaluation of ordinary oils and HD oils, as well as for selection tests conducted for research purposes.

Among the most common quick methods for testing oils are the L-4 method, using a Chevrolet automobile engine (United States), tests on a Fowler or "Petter" engine (Great Britain).

L-4 method. The test carried out on a six-cylinder carburetor-type Chevrolet engine is designed to determine the corrosiveness of an oil with respect to lead-bronze bearing linings. Tests last 36 hours.

TABLE 29. Comparative Evaluations of Various Oils for Their Tendency to Cause Ring Burning During Tests with Fowler Motor

1 Масло	2 Число часов работы двигателя до момента пригорания верхнего поршневого кольца
Масло без присадки 3 . . . . .	2
Масло с присадкой для тяжелых условий работы (серия 1) 4 . . . . .	14
То же, для особо тяжелых условий работы (серия 3) . . . 5 . . . . .	40

1) Oil; 2) number of hours of engine operation prior to burning of top piston ring; 3) oil without additives; 4) oil with additive, heavy-duty operation (series 1); 5) the same, for especially heavy-duty service (series 3).

The evaluation is made on the basis of the bearing weight loss. An oil satisfying the requirements of the MIL - 210ChA specification of the

United States Department of Defense should produce a weight loss not exceeding 100 mg per bearing.

Oils without additives, tested under such conditions, show bearing weight losses reaching 1000 mg.

Tests with single-cylinder Fowler diesel engine. This engine has been specially designed for evaluating the ability of oils with additives to prevent piston-ring burning. The top compression ring is moved close to the piston crown in order to speed up the onset of burning. The temperature in the top piston-ring groove reaches about

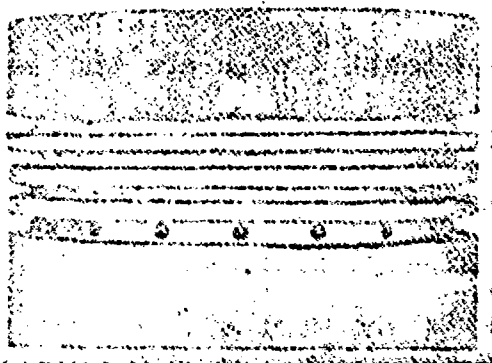


Fig. 24. Piston of Caterpillar engine following test with series 2 oil.

270°C. The test is continued until the top ring becomes gummed; the instant of gumming is determined from the increase in crankcase pressure that occurs owing to escaping gases from the combustion chamber. The oil is evaluated in terms of hours of engine operation before gumming of the top ring.

Table 29 gives comparative data for various oils on the basis of Fowler-engine tests.

In the United States, oil selection tests for research purposes are carried out also with the small Louison carburetor type engine (cylinder diameter 67 mm, piston stroke 70 mm) [12].

The tests are carried out in two forms:

a) in order to evaluate oil corrosiveness, 60 hours duration; here the oil is maintained at a high temperature of 138°C in the crankcase, with a cooling-fluid temperature of 99-100°C;

b) in order to evaluate piston-ring gumming, duration 100 hours; in this case, the temperature of the oil in the crankcase is 82°C,

while the cooling-fluid temperature (ethylene glycol is used) in the cylinder jacket is 177°C.

Extreme-pressure oils are given motor tests on Caterpillar engines for 480 hours.

A series 1 oil is tested in accordance with the L-1 method. For series 2 oils, tests are carried out in accordance with the 1D or L-5 methods, where conditions are considerably more rigorous than is the case with the L-1 method.

L-1 method. The test is carried out with a Caterpillar engine without supercharging; the tendency of the oil to form carbon and varnish is investigated, as is piston-ring gumming and over-all piston fouling. The test lasts 480 hours, with the oil changed every 120 hours.

For an oil to satisfy the stipulations of the MIL-4-2104 specification, the piston skirt and ring grooves must be completely clean, as shown in Fig. 24.

1D method. The test is carried out in a supercharged Caterpillar engine using fuel with a high sulfur content (0.95-1.05%); this test is used for oils that must satisfy the extremely rigid requirements of Supplement 2 of the MIL-104 specification.

The requirements for piston fouling are the same for oils tested by this method as when the L-1 method is used.

L-5 method. This method provides for a 500-hour test of the oil in a 2-cycle five-speed diesel engine with no oil change at maximum speed and load. The test is designed to evaluate the anticorrosion and detergency properties of an oil, the tendency of the oil to cause piston-ring gumming and bearing corrosion.

The method provides that samples of oil be taken and checked every 24 hours of operation; they may be used to evaluate oil service



TABLE 30. Basic Motor-Test Methods for Foreign Oils

1 Наименование и индекс методики испытания	2 Фоулер	L-4
4 Основная цель испытания	5 Оценка склонности масла вызывать пригорание поршневых колец	Оценка: 6 а) коррозии и подшипинок из свинцовой бронзы б) отложений на поршне
11 Продолжительность испытания, часы	12 До пригорания верхнего кольца	36
13 Наименование двигателя и его основные характеристики	14 4-тактный дизель Фоулер	15 4-тактный карбюраторный двигатель Шевроле
20 Число цилиндров	1	6
21 Диаметр цилиндров, мм	139,7	88,9
22 Ход поршня, мм	139,7	95
23 Мощность, э. л. с.	24	30
24 Число оборотов, об/мин	1500	3150
25 Среднее эффективное давление, кг/см <sup>2</sup>	7,0	—
26 Режим работы:		
27 температура воды на выходе, °C	85	93
28 температура масла, °C	75	138
29 смена масла, часы	32 Без смены	32 Без смены
30 Требования к топливу для испытаний:		
31 содержание серы, %	1,0	33 (Бензин)

1) Name and identification number of test method; 2) Fowler; 3) Petter AVI; 4) main purpose of test; 5) evaluation of tendency of oil to cause piston-ring gumming; 6) determination of: a) corrosion of lead-bronze bearing; b) deposits on piston; 7) determination of: a) deposits on piston; b) bearing corrosion; 8) determination of oil detergency (piston fouling); 9) the same; 10) evaluation of detergency and anticorrosion properties, and oil service life; 11) test duration, hours; 12) until top ring gums; 13) name of engine and basic characteristics; 14) four-cycle Fowler diesel; 15) 4-cycle carburetor-type Chevrolet engine; 16) 4-cycle Petter diesel; 17) 4-cycle Caterpillar diesel (without supercharging); 18) 4-cycle Caterpillar diesel with supercharging; 19) 2-cycle diesel; 20) number of cylinders; 21) cylinder diameter, mm; 22) piston stroke, mm; 23) power, effective horsepower; 24) speed, rpm; 25) mean effective pressure, kg/cm<sup>2</sup>; 26) operating conditions; 27) water temperature at outlet, °C; 28) oil temperature, °C; 29) oil change, hours; 30) specifications for test fuel; 31) sulfur content, %; 32) no change; 33) (gasoline); 34) (ethylene glycol); 35) no less than 0.35.

3 Petter AV1	L-1	1-D	L-5
7 Оценка: а) отложившийся на поршне б) коррозии под- шипников	8 Оценка мою- щих свойств мас- ла (чистота поршня)	9 То же	10 Оценка моющих и антикорроз- ионных свойств и срока службы масла
120 16 4-тактный дизель Паттер	480 17 4-тактный дизель Катерпиллар (без наддува)	480 18 4-тактный дизель Катерпиллар с наддувом	500 19 2-тактный дизель
1 80 110 3.3 1500 —	1 146 203 19.8 1000 5.27	1 146 203 42 1200 9.50	4 108 127 103 2000 —
34 120 (откачиваемый) 55 32 без смеси	82 65 120	93 80 120	82 — 32 без смеси
1.07	35 Не менее 0.35	0.95—1.05	—

life in the engine.

Table 30 gives engine characteristics and conditions for oil motor tests.

Oils for especially heavy-duty service (series 2 and 3) should, in the most critical cases, also undergo extended tests in full-size engines, under conditions approximating operating conditions.

Lubricating oils used for engines in the United States Navy undergo special tests in addition to standard tests such as the Caterpillar L-1 test. Thus, for example, series 2 oil designed to lubricate supercharged marine diesel engines operating under high loads and using high-sulfur fuel are tested for 480 hours (with no oil change) in a General Motors-71 engine operating with a fuel containing 1.0% sulfur with a cooling-water temperature of 50°C and a back pressure of 50 mm

Fig.

During the tests, at specific time intervals 2% sea water is added to the engine crankcase, simulating the actual conditions that may be encountered during operation of the marine diesel engine.

In order to satisfy the requirements of this very rigorous test, up to 10% or more of detergent and anticorrosion additives must be introduced into the oil.

In Great Britain, a Petter W-1 engine with spark ignition is used to check the quality of ordinary oils in place of the L-4 method. These tests last 36 hours with an oil temperature of  $138^{\circ}\text{C}$  and a cooling-fluid temperature of  $150^{\circ}\text{C}$ , i.e., the conditions are close to those of the L-4 test method using the Chevrolet engine.

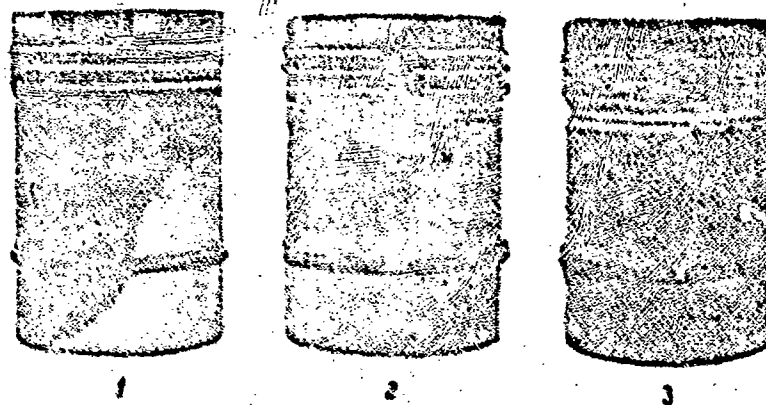


Fig. 25. Piston of Petter AVI diesel engine following operation with fuel containing 1.0% sulfur, for oils of various types. 1) Premium oil (no detergent additive); 2) HD-type oil for heavy-duty service; 3) HD series 2 oil, with high content of detergent additive.

In addition to the L-1 test with the Caterpillar diesel engine, a single-cylinder Petter AVI (Ch8.0/11) diesel engine is used in Great Britain to test oils for heavy-duty service. The test lasts 120 hours with no oil change, at a cooling-fluid temperature of  $120^{\circ}\text{C}$  and an oil temperature of  $55^{\circ}$ . An arbitrary scale is used to determine the amount of deposits, and the corrosiveness is evaluated from the weight loss

of the bearing linings.

Figure 25 shows the side wall of a Petter AVL diesel piston after operation with a high-sulfur fuel using oils with various types of additives.

Recently, the special CLR engine has been developed in the United States; it is designed to determine oil grade, but judging from the literature, this type of test has as yet not become very common.

## Chapter 4

### UTILIZATION OF OIL WITH ADDITIVES IN DIESEL ENGINES

#### RESULTS OF OIL AND ADDITIVE TESTS IN LOW COMBUSTION-INTENSITY DIESEL ENGINES

Low-intensity diesel engines with piston speeds not exceeding 6-7 m/sec and a mean effective pressure reaching 6 kg/cm<sup>2</sup> at piston temperatures near the top compression ring below 250°C, and place the least severe demands on oil quality. Oils with additives are used in these diesels primarily in order to avoid corrosion of the bearing alloys and to neutralize harmful combustion products of high-sulfur fuels.

The low combustion-intensity diesels include many low-speed unsupercharged marine engines, high-speed auxiliary marine or stationary diesels such as the Ch8.5/11 and Ch10.5/13 diesels, and the majority of automotive-tractor diesels (with the exception of certain types of diesel engines such as the YaAZ-206, SMD, etc.).

Tractor diesel engines, however, which make up nearly half the number of diesels in the Soviet Union, are the greatest consumers of fuels and oils.

The tractor fleet operates basically with diesel fuels containing up to 1.0% sulfur, and even more in individual cases. The characteristic feature of tractor-diesel operation is operation in dust-filled air, which is one of the factors causing severe contamination of the oil; thus problems of using oils with additives that decrease oil consumption by prolonging service life and the arrangement of oil filter-

ing for tractor diesels are of extreme importance.

The basic tractor-diesel oil grades are the diesel oils made to GOST 5304-54 and GOST 8581-57. Diesel oils, produced with TsiATIM-339 additive, are capable of providing reliable operation of low combustion-intensity tractor diesels when the fuels used contain no more than 1.0% sulfur.

The TsiATIM-339 additive, however, still is not effective enough, and does not meet the requirements for oils used in diesels supercharged to higher levels. The basic drawback to this additive lies in its limited detergency, since the additive cannot prevent considerable carbon formation and gumming of piston rings in high combustion-intensity engines.

TABLE 31. Effect of Additives on Properties of DS-11 Diesel Oil (Made from Sulfur-Bearing Crudes) as Determined on Laboratory Apparatus

1 Показатель	3 Без присадки	2 С присадкой				
		4 3% ЦИАТИМ-339	5 3% АЭНИН-7	6 4,5% ВНИИ ИП-22	7 6% ВНИИ ИП-350	8 8% ПМС-19
Зольность, % 9	0,02	0,33	0,33	0,44	0,91	0,60
Коррозийность по Пинкевичу (на свинец), г/м² 10	9,0	6,0	3,0	2,0	3,5	0,35
Термоокислительная стабильность по методу Шапел при 250°С, мин 11	16	35	35	72	97	Не окр.
Менюше свойства по методу ПЗВ, баллы 12	3,5	1,5	1,5	2,0	0,5	0

1) Characteristic; 2) with additive; 3) without additive; 4) 3% TsiATIM-339; 5) 3% AzNII-7; 6) 4.5% PNI IP-22; 7) 6% VNII NP-350; 8) 8% PMS-19; 9) ash, %; 10) corrosion, Pinkevich method (on lead) g/m<sup>2</sup>; 11) thermal-oxidation stability, Papok method, 250°C, min; 12) detergency, PZV method, arbitrary units.

The AzNII-7 alkylphenol additive has somewhat better detergency and antiwear properties, but nonetheless it should also be classified

TABLE 32. Results of 100-Hour Tests of Domestic and Foreign Oils with Additives in D-35 Engine (Using Fuel Containing 1% Sulfur)

1 Показатель	2 Масло ДС-11			6 Kastrol SAE-30 HD	7 Rimula Shell SAE-30 HD
	3 +3% TsIATIM-339	4 +6% VNII NP-360	5 +10% PMS-19		
Износ гильз, мк . 8 . . .	6.1	3.8	3.8	3.3	3.3
Потеря веса колец, % 9 . .	1.1	0.6	0.6	0.8	0.8
Количество нагара на поршнях и кольцах, % 10 . . .	12	6	4	2.8	3.3
Поверхность поршня, покрытая лаком, % 11 . . .	50	30	0	0	0

1) Characteristic; 2) DS-11 oil; 3) +3% TsIATIM-339; 4) +6% VNII NP-360; 5) +10% PMS-19; 6) Kastrol, SAE-30 HD; 7) Rimula Shell SAE-30 HD; 8) sleeve wear, microns; 9) ring weight loss, g; 10) amount of carbon on pistons and ring, %; 11) piston surface, % covered with varnish.

as an oil additive suitable for diesels with little or moderate supercharging.

Table 31 gives results of tests of DS-11 diesel oil with various additives, using laboratory apparatus. These data show a considerable improvement in detergency and anticorrosion properties of the oil following introduction of the additives.

Table 32 compares results of short-term tests of domestic oils with additives and test results for the best foreign specimens.

The data given in Tables 31 and 32 show that oils with the new phosphorus-containing VNII NP-360 and MVI IP-22 additives, as well as with the Type PMS-19 sulfonate additives, are considerably more effective than the TsIATIM-339 or AzNII-7 alkylphenol additives, and in many characteristics approach the foreign oil designed for heavy-duty service such as "Kastrol" or "Rimula Shell."

In analyzing the results of oil motor tests, the question naturally arises as to whether it is possible to increase the effectiveness of additive action by increasing the concentration of the addi-

tive in the oil.

Figure 26 due to N.G. Puchkov [36] shows results of wear measurements on piston rings and the top zone of cylinder sleeves for a YaAZ-204 diesel as a function of fuel sulfur content and concentration of TsiATIM-339 additive in the diesel oil.

As the chart shows, the engine wear curves for oils with 3 and 5% additive intersect at points corresponding to fuel sulfur contents of 0.8-1.0%.

It follows from this that when a YaAZ-204 engine is operated with a fuel containing less than 1.0% sulfur, an increase in the concentration of an additive of the TsiATIM-339 type over 5% not only does not decrease wear, but may actually lead to the opposite result in individual sections owing to an increase in abrasive wear.

Foreign authors [57] have already commented on the appearance of abrasive wear in an engine with an extremely high oil additive content.

On the other hand, when high-sulfur and especially heavy fuels are used, an increase in additive content is required. This is indicated by the widespread utilization abroad of especially heavy-duty oils with additive contents reaching 15-20%.

A series of tests have been carried out at the Central Diesel Scientific Research Institute, using Type Ch10.5/13 engines in order to obtain a relative evaluation of the effectiveness of various oil additives [30, 31].

The tests were carried out with GOST 305-58 diesel fuel (sulfur content, 0.8%), and a heavy high-sulfur fuel containing 1.6% sulfur.

The engine operated normally with both fuels, but examination of engine condition and amount of wear after 150 hours of operation showed a considerable difference in wear and in the quantity of depos-



its following operation with fuels containing 0.8 and 1.6% sulfur.

Ring wear was determined by weight and sleeve wear by the crescent method; in addition, total engine wear was calculated on the

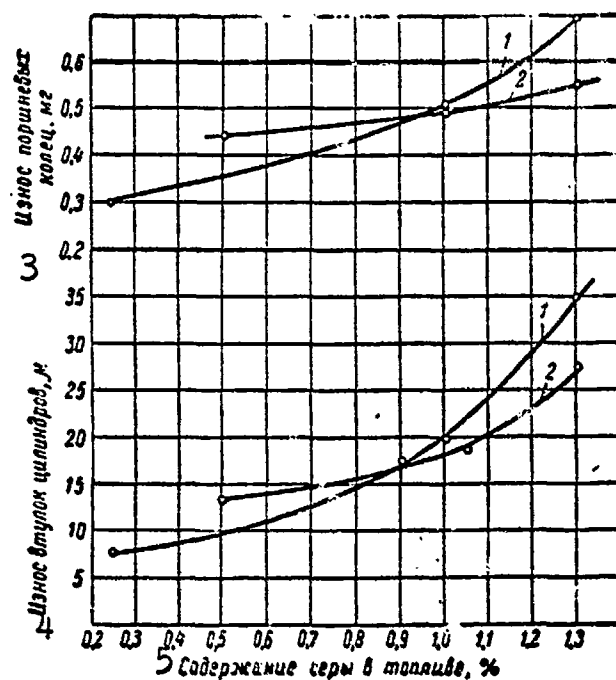


Fig. 56 Wear on YaAZ-204 engine as a function of oil additive concentration, for fuels with various sulfur contents. 1) 3% TsiATIM-339; 2) 5% TsiATIM-339; 3) piston-ring wear, mg; 4) cylinder-sleeve wear, microns; 5) fuel sulfur content, %.

basis of a determination of the oil iron content. The results given in Table 33 show that when the engine was changed over from a standard fuel, with 0.8% sulfur, to a high-sulfur fuel and D-11 oil with no additives was used, piston-ring wear rose by a factor of 1.8, and sleeve wear by a factor of 3.5. There was also an increase in the amount of carbon and varnish.

The utilization of oil additives, and in particular of the phosphorus-containing VNII NP-360 and MNI IP-22 additives resulted in a considerable decrease in wear and amount of deposits; the sleeve wear, however, still exceeded the amount of wear found when the engine was

TABLE 33. Results of Oil Additive Tests, 4Ch10.5/13 Engine Operating on High-Sulfur Fuel (Test Duration, 150 Hours)

1 Топливо	2 Масло-присадка	3 Износ (средние данные по 4 цилиндрам)				7 Оценка лака и нагара			
		4 Верхнее поршневое кольцо	5 Суммарный износ всех колец		6 Средний износ втулки	8 Общий износ (по определению железа в масле)		9 Количество горевших колец	10 Поверхность юбки поршня, покрытая лаком
		13	ε	%	μ	ε	%		
Дизельное (содержание серы 0,8) 11	Д-11 без присадки 12	0,42	100	0,70	16	100	2,8	19 1 (частично)	15
Высокосернистое (содержание серы 1,5%) 13	Д-11 без присадки 14	0,56	135	1,24	58	260	7,3	1	30-40
	Д-11 + 5% АЗНИИ-7 15	0,47	110	0,77	45	280	4,5	0	10-15
	ДС-11 без присадки 14	0,59	115	0,81	40	250	4,4	6	60
	ДС-11 + 4,5% АЗНИИ-7 16	0,32	76	0,65	24	150	2,0	2	20
	ДС-11 + 6% ВНИИ НП-360 17	0,26	62	0,50	27	170	2,2	0	10-15

1) Fuel; 2) oil-additive; 3) wear (mean data for four cylinders); 4) top piston ring; 5) total wear on all 6 rings; 6) mean sleeve wear; 7) varnish and carbon determination; 8) total wear (determined from iron in oil; 9) number of gummed rings; 10) surface of piston skirt covered with varnish; 11) diesel (sulfur content, 1.5%); 12) D-11, no additives; 13) high-sulfur (sulfur content, 1.5%); 14) D-11, no additives; 15) D-11 + 5% AZNII-7; 16) DS-11 + 4.5% MNI IP-22; 17) DS-11 + 6% VNI NP-360; 18) E; 19) in some cases.

operated with standard fuel.

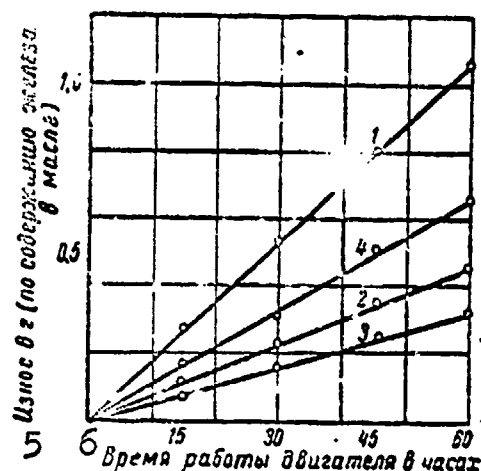


Fig. 27. Total engine wear as a function of type of fuel and oil additive (wear lines). 1) High-sulfur fuel ( $S = 1.6\%$ ), DS-11 oil without additive; 2) the same, DS-11 oil + 4.5% MNI IP-22; 3) the same, + 6% VNI NP-360; 4) diesel fuel ( $S = 0.8\%$ ), DS-11 oil without additive; 5) wear, g (from iron content); 6) engine operating time, hours.

Figure 27 shows wear lines plotted on the basis of a study of the dynamics of iron-content increase in the crankcase oil of a Ch10.5/13 engine when various oil additives were used.

Tests using a Ch10.5/13 engine and fuels with various sulfur contents were also carried out by M. S. Smirnov [43].

The series of tests of oil additives and fuels with various sulfur contents in Ch10.5/13 engines shows that for the most vulnerable part of the engine - the cylinder sleeve - the wear per 1000 hours of operation with a low-sulfur fuel amounts to about 75 microns in the upper zone.

As we can see from the curve given in Fig. 28, when a fuel with a 0.8-1.0% sulfur content was used instead, sleeve wear rose to 130-160

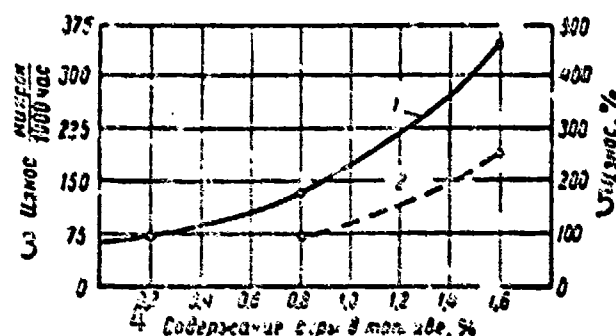


Fig. 28. Wear on cylinder sleeve of Ch10.5/13 engine as a function of fuel sulfur content and oil additive. 1) Oil without additive; 2) the same, VNI NP-360 additive; 3) wear, microns/1000 hours; 4) fuel sulfur content, %; 5) wear, %.

microns. By using diesel oil with VNII NP-360 additive, wear could be reduced to 75 microns.

Thus, by using oil additives of the phosphorus-containing VNII NP-360 type or other less effective additives, cylinder-sleeve wear can be reduced to the level of wear with a low-sulfur fuel (containing 0.2% sulfur) when the engine uses a fuel containing up to 1.0%.

As far as high-sulfur diesel fuels are concerned (containing more than 1.0% sulfur) they can be used in high-speed diesels with no decrease in motor potential if an entire set of measures is carried out, i.e., effective oil additives, fuel additives, protective coating, etc., are used simultaneously.

The results of selection tests have made it possible to recommend the tested additives for diesel factory tests in more heavily supercharged diesel engines of various types using high-sulfur fuels containing no more than 1.0% sulfur.

#### OIL SERVICE LIFE IN ENGINE AND CONSUMPTION OF ADDITIVES

Oil service life in an engine. The problem of the maximum permissible oil service life in an engine is of primary importance, since too-frequent oil changes lead to enormous waste of oil, while if spent oil is not changed soon enough, excessive wear and engine fouling will result.

As we have already mentioned, a certain portion of the oil reaches the maximum-temperature zone at the top of the piston, and is subjected to severe thermal decomposition with the formation of carbon-bearing products known under the common name of carbon scale and varnish. When this happens, is there a radical change in the structure of the hydrocarbons in the basic portion of the oil that does not have extensive contact with the very hot surfaces of the cylinder-piston system? Studies carried out by G.V. Vinogradov [8], as well as N.G. Puchkov and

M.S. Borova [37] have shown that despite the oil-oxidation processes that are going on and some accumulation of polycyclic compounds, on the whole, the hydrocarbon-group chemical composition of the oil changes very little. Thus, we may assume that if there is adequate elimination of all contaminants, including thermal-decomposition products as well as engine-wear products, the chemical composition of the spent oil will differ little from that of fresh oil over an extended service period. This fact raises the problem of prolonging oil service life in the engine by arranging for effective filtering during the operating process.

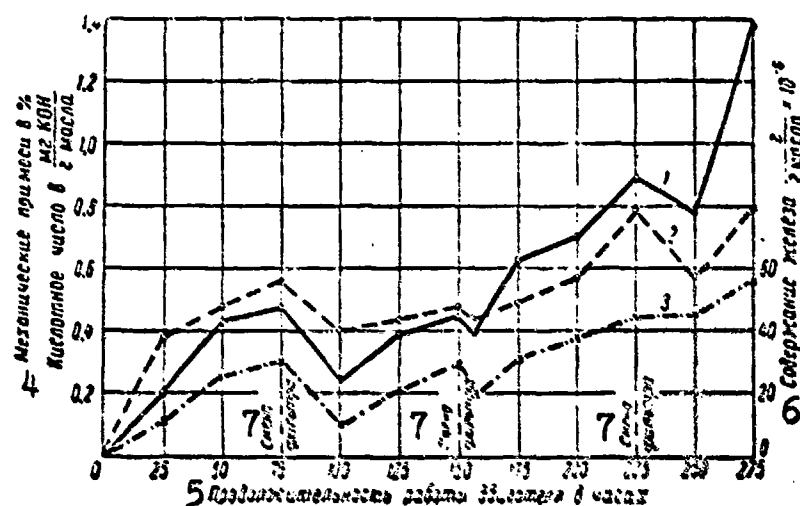


Fig. 29. Variation in diesel-oil performance characteristics during operation of 4Ch10.5/13 oil with filter changed every 75 hours (no oil change). 1) Mechanical impurities; 2) acid number; 3) iron content; 4) mechanical impurities, %, acid number, mg KOH/g of oil; 5) duration of engine operation, hours; 6) iron content, g/g of oil ( $\times 10^6$ ); 7) filter change.

For the majority of automotive and tractor engines, as well as for many marine and stationary diesels of up to 500 horsepower, the factory instructions call for a change of crankcase oil every 100-120 hours of engine operation. It should be noted that at the present time there are no oil quality indicators with scientifically-established

limiting values which when reached indicate that the oil should be removed from the engine lubrication system and fresh oil supplied.

In regular operating practice for high-speed diesel engines, the oil is normally changed on the basis of the fact that the mechanical-impurity content should not exceed 0.4-0.5% and the acid number should not exceed 0.5 mg KOH per gram of oil. Thus, for example, in YaAZ-204 automotive diesels, the oil is changed every three thousand or four thousand kilometers, i.e., after about 100 hours of engine operation. Here the characteristics of Dp-11 oil have the following values: mechanical impurities, 0.17-0.36%; acid number, 0.2-0.6 mg KOH per gram of oil.

When an engine uses high-sulfur fuel, the oil ages at a faster rate.

The acidity and mechanical-impurity content of crankcase oil may be reduced by changing the fine oil filters more often, or by using additional centrifuge filtering [30].

Figure 29 shows the variation in certain characteristics of DS-11 diesel oils during tests with a 1Ch10.5/13 diesel, carried out by the author, using a fuel containing 1.6% sulfur over a 275-hour period with no oil change, but with the type ASFO fine oil filters changed every 75 hours [30].

As the nature of the curves or the change in oil characteristics shows, with the engine operated on a high-sulfur fuel, by the time the engine has been operated for 75 hours, the oil showed very high values for acidity, mechanical impurities and iron content, and required changing. With the filter changed every 75 hours of operation, with no oil change, not only were the oil indices held to permissible levels, but the service life was prolonged to 150-200 hours, which is completely justifiable from the point of view of economics.

S.V. Ventsel' assumes that the accumulation of organic impurities in the oil has no effect on engine wear, since the wear is caused primarily by the abrasive action of the mineral portion of the contaminants. Organic compounds such as gums create a shell about the solid particles of iron or silicon, and play a positive role in decreasing abrasive wear. Thus, according to Ventsel', oil filtering should consist primarily in removing the mineral portion of the contaminants, i.e., sand, wear products, etc., which is best done by means of centrifuge.

In recent years, several tests have been carried out with tractor diesels, using centrifuge filtering or more frequent changing of filter elements. The tests were aimed at decreasing wear and prolonging the service life of the lubricating oil [4, 21].

All of the tests carried out show that:

- a) centrifuge oil filtering considerably decreases engine wear;
- b) by changing filtering elements more frequently, oil service life may be prolonged from 100-120 to 240-360 hours, producing an oil savings of up to 25-30%.

On the basis of the results of the tests carried out, many tractor factories have replaced the fine oil filters in the diesels produced with centrifuge filters. These considerations, however, which support the superiority of centrifuges over fine oil filters apply to the reduction of abrasive wear, and do not fully take into account the harmful effect of tarry products, which intensify carbon and varnish formation in the engine. Thus, a more reliable method of oil filtering for diesels would be the utilization of fine filters in conjunction with centrifuges; as a result, both the acid tarry products and the mineral particles causing abrasive wear would be removed from the oil.

Additive consumption. During operation of an engine, the multi-

purpose additive contained in the oil is gradually used up as it reacts with oil oxidation products and acid products of fuel combustion, and it is replenished under operating conditions only when fresh oil

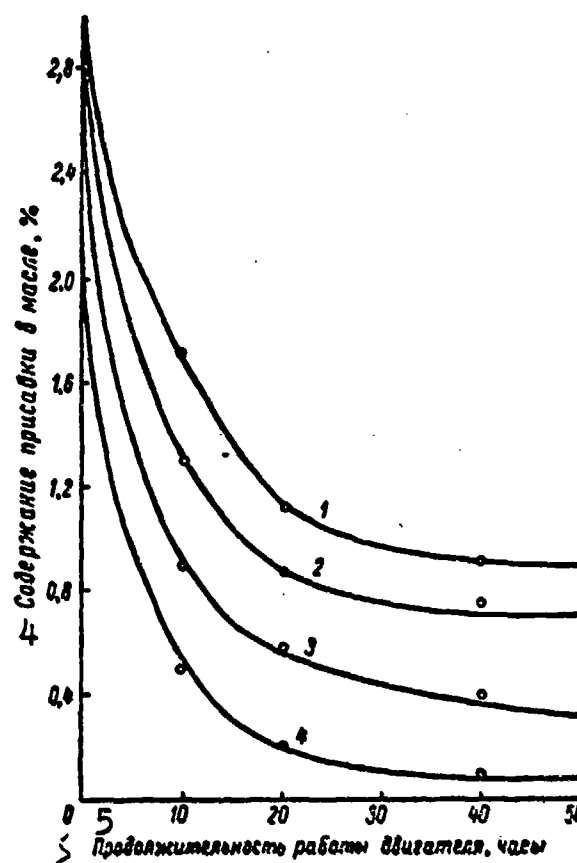


Fig. 30. Effect of fuel sulfur content on consumption of TsIAT-IM-339 additive (YaAZ-204 diesel). 1) Fuel with 0.2% sulfur content; 2) the same, 0.5% sulfur content; 3) the same, 1.0% sulfur content; 4) the same, 1.3% sulfur content; 4) oil additive content, %; 5) duration of engine operation, hours.

is added.

A rough idea of the additive content of an oil may be obtained from the oil ash content, and a more precise idea from an analytical determination of the special components of the given additive, such as barium, calcium, or phosphorus [21, 45].

The actual mechanism that uses up additives has not been defi-



nitely established; it may be assumed, however, that the basic factors for additive consumption are:

- 1) adsorption of additives on particles of undissolved contamination products and retention of the contaminants by oil filters (centrifuges) together with the adsorbed additive;

- 2) direct adsorption of the additive by the filtering elements in the oil filters.

These ideas have been confirmed by numerous experiments carried out under bench conditions.

A.B. Vipper [9] assumes that in addition to the factors mentioned, interaction of detergent additives with the surfaces of engine parts accounts for a considerable amount of additive loss.

This conclusion follows from the fact that the decrease in oil additive concentration is most noticeable during the first few hours of engine operation.

The higher the fuel sulfur content, the more rapidly the additive is used up.

This is explained by the fact that as the fuel sulfur content goes up, there is an increase in the amount of acid products in the oil, and a rise in the amount of additive needed to neutralize the acid products and disperse the carbon particles. Figure 30 shows results obtained by N.G. Puchkov [35] in a study of the consumption of TsIATIM-339 additives using a YaAZ-204 diesel engine and fuels of various sulfur contents.

N.I. Itinskaya and M.D. Degtyarev [21] have studied the variation in the properties of Dp-14 diesel oil with TsIATIM-339 additive during operation of DT-54 tractors, with oil changes every 120 to 360 hours. The additive content was monitored by determining the ash content, as well as the oil barium and sulfur content.

Figure 31 shows the decrease in oil ash and barium content; from this it is possible to obtain a rough idea as to additive consumption when the engine is operated for 360 hours with no oil change.

As the nature of the curves shows, the additive is consumed most rapidly over the first 60 hours of engine operation, after which the content remains more or less stable.

In this case also, no noticeable deterioration in oil detergency properties is observed.

It has been established that oil oxidation occurs most vigorously during the first 60-120 hours of engine operation, since it is primarily the most unstable hydrocarbons that oxidize during this period. The alkylphenols that react with the additive to form organic acids retard the oxidation process and prevent the oxidation products that do form from coagulating.

The need for broad-scale utilization of centrifuges and fine oil filters raises the problem of whether or not these filtering devices will remove the additive from the oil.

A very small quantity of additive may be adsorbed on the surfaces of a new Type ASFO cardboard filter; in the main, however, the additive will be trapped together with carbon deposits, in proportion to the quantity, having thus first carried out its dispersing function.

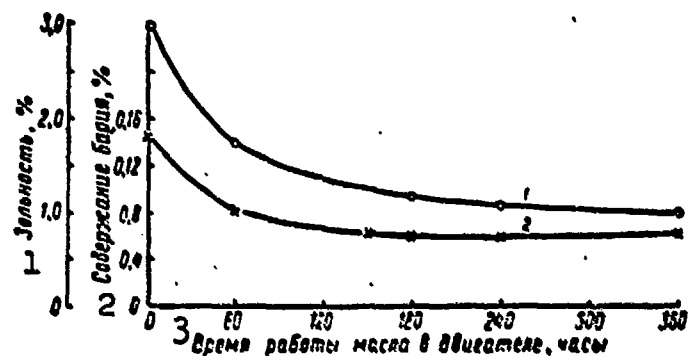


Fig. 31. Variation in ash content (1) and barium content (2) of oil during engine operation. 1) Ash, %; 2) barium content, %; 3) oil service period in engine, hours.

A.B. Vipper, O.S. Obleukhova, and others [33] have studied the effect of centrifuge filtering on the removal of additives from oil. In their test using an automobile engine provided with a centrifuge, the oil additive content and the additive content of the deposits were checked by determination of the main additive content (barium or calcium metals).

The results of 100-hour oil tests with TsiATIM-339, MNI IP-22 additives, and others, showed that relatively little additive was retained in the centrifuge deposits, ranging from 21-28% of the initial oil additive content.

In 150-hour tests carried out by the author with a 4Ch10.5/13 engine, using D-11 oil with AzNII-7 additive, the total amount of additive in the fine-filter deposits and in the centrifuge amounted to 13.6% of the total amount of additive present in the oil [32]. Thus, the utilization of fine filters and a centrifuge in no way interferes with the utilization of oils with additives.

Operating practice for certain marine installation calls for washing of the circulating oil with hot water or steam and subsequent separation of the water in separators. In this case, some of the additive may be lost through the formation of solutions or emulsions in the water.

#### CHOICE OF OILS AND ADDITIVES FOR SUPERCHARGED DIESELS

Testing additives for locomotive diesels. In connection with the development of diesel locomotive construction, the requirements of the railway industry for diesel fuels has risen sharply. It has thus become necessary to ensure that the fleet of diesel locomotives can use fuels and oils obtained by refining sulfur-bearing Eastern crudes with no loss of engine reliability or service life.

In order to solve this problem, several bench and operating tests

were carried out with a 2D100 engine, which presently is the chief engine type used for main-line diesel locomotives; it was operated with fuel and oil from sulfur-bearing crudes and various additives were



Fig. 32. Exhaust ports of 2D100 diesel following operation with high-sulfur fuel and DSp-11 fuel. 1) Low-sulfur fuel, D-11 oil; 2) high-sulfur fuel, DS-11 oil with VNII NP-360 additive; 3) the same, TsIATIM-339 additive.

used.

The 2D100 diesel locomotive engine is a two-cycle 10-cylinder diesel engine with opposed pistons developing 2000 horsepower at 850 rpm.

The 2D100 diesel is an engine with very great combustion intensity. The engine pistons are oil cooled. The maximum crown temperature reaches  $520^{\circ}\text{C}$ , while the inside surface of the crown, over which the oil flows, has a temperature that fluctuates from 190 (at the center) to  $260^{\circ}\text{C}$  (at the periphery). Thus, the 2D100 is characterized by considerable amounts of carbon formation; when high-sulfur fuels are used, this leads to the formation of carbon residue and decreases the available cross section of the cylinder scavenging and exhaust ports.

TABLE 34. Results of Bench Tests of Oil Additives with 2D100 Engine

1 Топливо	2 Масло и присадка	3 Нагарообразование				4 на поверхности поршня, покрывающей лаком, %		8 в кольцевых поршневых кольцах	9 на выхлопных окнах	10 на продувочных окнах	11 Общее количество пригоревших колец, шт.		Износ цилиндра, 14 м	
		5 верхнее	6 нижнее	7 в выхлопных окнах	12 полностью	13 частично	14 V пояс				15 V пояс	16 V пояс		
17 Дизельное Гост 4749-42 (содержание серы 0,2%)	21 АЗНИИ-7 (базисное) + 3%	100	100	5,7	12,2	4,4	0	0	54	50				
18 Дизельное Гост 305-42 (содержание серы 1,2%)	22 АЗНИИ-7 (из сернистых нефтей) + ЦИАТИМ-139	40	60-80	12,0	32,0	7,0	5	10	90	76				
19 То же	23 АЗНИИ-8	25	70-80	8,9	51,4	17,6	0	4	246	289				
20 Дизельное Гост 305-42 (содержание серы 1,0%)	24 АЗНИИ-13,7 МНИИ НП-22	15	60	7,2	45,7	8,4	2	10	85	86				
	25 АЗНИИ-13,7 МНИИ НП-300	30	60	10,4	26,4	31,4	1	2	85	70				
	26 АЗНИИ-13,7 МНИИ НП-300	15-20	30-40	9,5	57,2	11,7	0	4	154	163				
	27 АЗНИИ-13,7 МНИИ НП-300	30	30	8,7-10,7	49,8	14,1	0	1	47	50				

1) Fuel; 2) oil and additive; 3) carbon formation; 4) on surface of piston skirt, % covered by varnish; 5) top; 6) bottom; 7) amount of carbon, g; 8) in piston-ring grooves; 9) on exhaust ports; 10) on scavenging ports; 11) total number of gummed rings; 12) completely; 13) partially; 14) sleeve wear, microns; 15) zone IV; 16) zone V; 17) GOST 4749-42 diesel fuel (sulfur content 0.2%); 18) GOST 305-42 diesel fuel (sulfur content 0.2%); 19) GOST 305-42 diesel fuel (sulfur content 1.2%); 20) the same; 21) GOST 305-58 diesel fuel (sulfur content 1.0%); 22) D-11 (Baku) + 3% AzNI-7; 23) D-11 (from sulfur-bearing crudes) + TsiATIM-339p; 24) D-11 + 8% AzNI-8; 25) D-11-13.7 MNI IP-22; 26) D-11 + 6% VNI NP-360.

to gumming of the piston rings, the formation of varnish deposits on the piston skirt with deposition of carbon in the ring grooves and on the inside surfaces of the piston, washed by the oil.

Figure 32 shows exhaust ports of the engine after operation with a sulfur-bearing fuel. The carbon deposited on the piston-head walls washed by the oil helps to raise the piston temperature. According to V.V. Arinkin [3], the carbon deposited during the first 150 hours of diesel operation raises piston temperature by  $65^{\circ}\text{C}$ .

The increased carbon formation and inadequate oil circulation caused the pistons to overheat, which may result in the formation of cracks in the piston crown. Conversion of an engine to sulfur-bearing-fuel operation, especially in conjunction with DS-11 diesel oil refined from sulfur-bearing crudes results in a considerable increase in the amount of carbon and varnish deposited, and makes it necessary to use effective detergent and antiwear additives with the oil.

Factory bench tests of various additives have been carried out with a 2D100 diesel operating on a diesel fuel containing 1.0 and 1.2% sulfur for periods of 600 hours for each additive tested (Table 34). To establish a standard, a 600-hour test was run with a 2D100 engine using a low-sulfur fuel and Baku D-11 oil with 3% AzNII-7 additive [42].

Tests and operating experience with 2D100 diesels have shown that when low-sulfur fuels and Baku oils are used, little carbon is formed.

A maximum cylinder-sleeve wear of 50 microns, and no ring gumming was found in the low-sulfur fuel tests. Where the engine was tested with a sulfur-bearing fuel and oil with TsiATIM-339, AzNII-8, and MNI IP-22 additives, unsatisfactory results were obtained. Sleeve wear with the high-sulfur fuel increased by a factor of 1.5 or more, reach-

ing values of 85-95 microns in zones of maximum wear.

The best values for decreased wear and carbon formation were given by VNII NP-360 additive. Here, as tests have shown, the question of the concentration of the additive in the oil is extremely important. As the data of Table 34 show, if the concentration of VNII NP-360 additive is raised from 6 to 15%, there is some increase in cylinder-sleeve wear due to the abrasive action of the large number of mineral compounds introduced into the oil along with the additive. Optimum results were obtained when DS-11 oil with 8% VNII NP-360 additive was used. Here wear and carbon formation in the 2D100 diesel, using fuel with a 1.0% sulfur content, corresponded to the values obtained during the reference tests with a low-sulfur fuel and Baku D-11 oil with 2VNII NP-360 additive (Fig. 33).

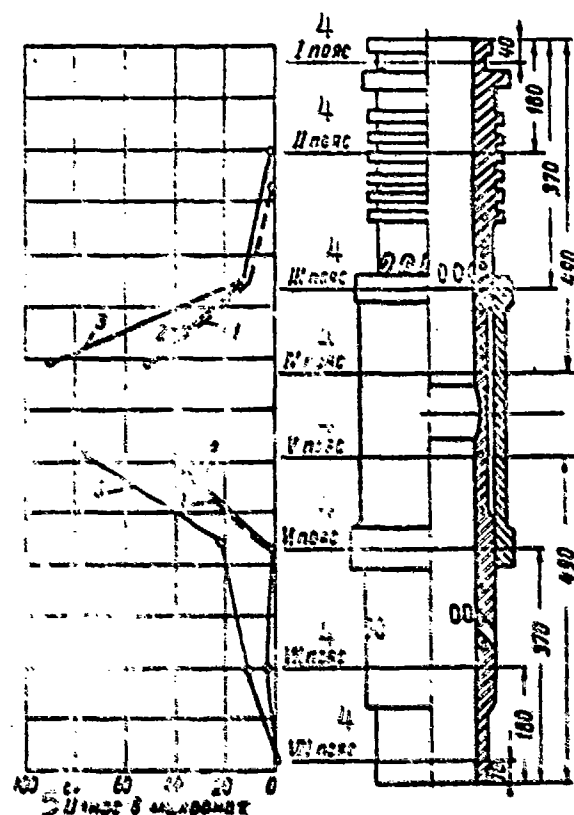


Fig. 33. Wear of sleeve of 2D100 diesel during bench tests with various fuels and oils. 1) low-sulfur fuel, DP-11 oil; 2) sulfur-bearing fuel, DS-11 oil with VNII NP-360 additive; 3) sulfur-bearing fuel, DS-11 oil with LUBRATIN-339 additive; 4) zone; 5) wear, microns.

Operating tests with high-sulfur fuels were carried out in TE-3 diesel locomotives. The basic material in the tests was the high-sulfur GOST 305-7 with up to 1.0% sulfur content and DS-11 oil

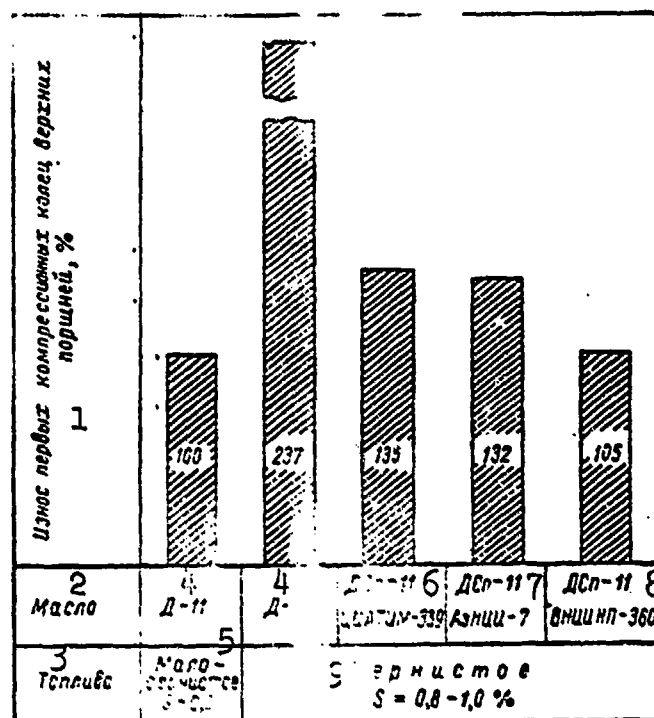


Fig. 34. Wear on piston rings of 2D100 diesel operated with oils having various additives. 1) Wear on first compression ring of top pistons, %; 2) oil; 3) fuel; 4) D-11; 5) low-sulfur, S = 0.2%; 6) DSp-11, TsIATIM-339; 7) DSp-11, AzNII-7; 8) DSp-11, VNII NP-360; 9) high-sulfur, S = 0.8-1.0%.

with VNII NP-360, TsIATIM-339p, and AzNII-7 additives. All of the test results obtained were compared with corresponding data for reference diesel locomotives using fuel with 0.2% sulfur content and D-11 Baku oil (GOST 5304-74). Each oil specimen was tested in three diesel locomotives with a total run of 120,000 km. Operating tests of DS-11 oil with TsIATIM-339 and AzNII-7 additives gave less satisfactory results.

Figure 34 shows comparative values for piston-ring wear in operating tests with a 2D100 diesel using diesel oils with various additives [18].



The results of tests of DS-11 oil with VNII NP-360 additive showed that the condition of the 2D100 engine following operation with a high-sulfur fuel was no worse with respect to wear or piston-ring gumming (Table 35) than that of the engine of a reference diesel locomotive that used a low-sulfur fuel and D-11 Baku oil. There was a slight exception to this statement in that the scavenging ports bore an increased amount of carbon deposit, making it necessary to clean them at least every 40-50 thousand km.

The tests carried out with diesel fuel containing up to 1.0% sulfur and DS-11 oil with 8% VNII NP-360 additive in diesel locomotives permitted the Ministry of Railways to recommend that these types of fuels and oils be introduced.

Tests of additives for high-speed marine diesel engines. The navy is one of the major consumers of diesel fuel; it is thus extremely important to make it possible to use sulfur-bearing fuels in marine diesels without decreasing reliability or service life. In this connection, several operating bench tests have been carried out recently for various types of marine diesels using oils with additives.

In all tests of a sulfur-bearing fuel containing up to 1.0% sulfur with no oil additives, increased wear and carbon deposits were noted. When diesel oil with TsiATIM-339 additive was used, wear and carbon in the types of engines mentioned corresponded roughly to the values measured when a low-sulfur fuel was used in operation. As an example, we may cite the results of 500-hour tests with a 3D6 engine (see Table 36). It is clear from these data that the utilization of TsiATIM-339 additive yielded some decrease in carbon deposition when the engine used a fuel containing no more than 1.0% sulfur; when the fuel contained more sulfur, however, the detergent action of this additive proved insufficiently effective.

TABLE 35. Basic Results of Operating Tests with 2D100 Diesels Running on High-Sulfur Fuel and Oil with VNII NP-360 Additive (from Data of I.S. Zelenetskiy)

1 Топливо и масло	2 Потери живого сечения продулочных окон, %	3 Количество пригоревших колец		4 Количество нагара в зоне поршневых колец	5 Износ	
			%		6 верхнего поршневого кольца, г	7 гильз и поясе-максимального износа, мм
8 Малосернистое (содержание серы 0,2%) . . . . .	5-8	10*	2,4 5,95	22,4 26,3	6,5	0,048
9 Масло Д-11					9,6	
10 Сернистое (содержание серы 0,8-1,0%) Масло ДС-11 8% VNII NP-360	20-30	6	1,5	15,9	6,8	0,050
11						

1) Fuel and oil; 2) loss in available scavenging-port cross section, %; 3) number of gummed rings; 4) amount of carbon in piston-ring zone, g; 5) wear; 6) top piston ring, g; 7) sleeve in zone of maximum wear, mm; 8) low-sulfur (0.2% sulfur content); 9) D-11 oil; 10) high-sulfur (0.8-1.0% sulfur content); 11) DS-11 oil, 8% VNII NP-360.

TABLE 36. Wear on Basic Parts of 3D6 Diesel After 500 Hours of Operation as a Function of Fuel Sulfur Content and Oil Additive (from Data of M.S. Smirnov)

1 Топливо	2 Масло	4 Нагар на днище поршня, г	3 Износ				
			5 поршневых колец, г	6 цилиндров, мм	вкладышей подшипников, мм		
					8 основных	9 шатунных	
10 Дизельное (содержание серы 1,0%)	МН-2 без	1,1	0,25	17	16	8	
11 То же	То же 3%	2,1	0,07	7	11	5	
То же (содержание серы 1,25%) 12	МН-2М-339 То же 11.	1,2	0,17	26	22	10	

1) Fuel; 2) oil; 3) wear; 4) carbon on piston crown, g; 5) piston rings, g; 6) cylinder sleeves, microns; 7) bearing linings, microns; 8) base; 9) connecting-rod; 10) diesel fuel (1.0% sulfur content); 11) the same; 12) the same (sulfur content 1.25%); 13) MK-22, no additives; 14) the same, + 3% TsiATIM-339.

Extended operating tests with M-50, 3D6, 9D and other marine diesel engines showed that it was possible to operate these engines temporarily with fuels containing up to 1.0% sulfur and an oil with TsIA-TIM-339 additive prior to the organization of broad-scale industrial production of more effective oil additives.

Tests with Type 40D engine. The 40D marine engine is a heavily supercharged engine. Tests with a low-sulfur fuel and the mixture recommended by the factory of D-11. Baku oil and MK-22 aviation oil and TsIATIM-339 additive showed that the engine remained in completely satisfactory condition. This test was taken as a reference test.

A series of 100-hour tests of this diesel engine with a high-sulfur fuel (containing about 1.0% sulfur) and DS-11 oil with various oil additives showed that in all cases the condition of the engine was poorer than it was following the reference tests (Table 37). Thus, for example, after tests of the PMS-19 oil additive, a decrease in piston-ring wear was noted together with a small amount of varnish deposits; the number of gummed rings, however, proved very high.

Thus, the tests showed that in order to make it possible to operate a 40D engine with fuels and oils refined from high-sulfur crudes, it is necessary to develop more effective additives than the test specimens. Until the new additives have been created, Type 40D supercharged diesel engines should be operated on low-sulfur fuel.

#### SPECIAL CYLINDER OILS

Modern diesel-powered vessels are equipped with large diesel plants of from 5-6 thousand to 20,000 horsepower in the unit and speeds of 120 rpm. These engines are low-speed crosshead-type diesel with a separate lubricating system. The high-power marine diesels include engines of the Burmeister and Wain, Doxford, MAN, Sulzer, and other types. A tendency characteristic of the operation of low-speed marine

TABLE 37. Results of Tests of Sulfur-Bearing Fuel and Additives in 40D Engine (Test Duration 100 Hours)

1 Топливо	2 Масло и присадки	3 Зольность масла, %	4 Напос верхнего компрессионного кольца, g	5 Количество пригоревших поршневых колец, шт.			9 Общее количество нагара на поршне, g	10 Поверхность поршня, покрытая лаком, %
				6 полностью или на дуге 180°	7 частично	8 всего		
1. ДС ГОСТ 4749-49 (содержание серы 0,2%) 12 ГОСТ 305-38 (содержание серы 1,0%) 13 То же	14 Д-11 + МК-22 + 3% ЦИАТИМ-339 15	0,2	1,4	0	5	5	14	60-65
	ДС-11 + 6% ВНИИ НП-360	0,8	1,8	0	18	18	19	35-40
	То же + 6% ВНИИ НП-371	0,6	1,7	8	9	17	19,5	50-55
	17. + 8% МНИ ИП-22	0,9	1,7	5	5	10	22	30-35
.	18. + 8,5% ПМС-19 . .	1,52	0,6	13	17	30	14	20-25
	19. + 15% ИГ-102у . .	1,22	1,0	23	2	25	20	70-75

1) Fuel; 2) oil and additive; 3) oil ash content, %; 4) wear on top compression ring, g; 5) number of gummed piston rings; 6) completely or over 180° arc; 7) partially; 8) total; 9) total amount of carbon on piston, g; 10) surface area of piston covered with varnish, %; 11) DS GOST 4749-49 (0.2% sulfur content); 12) GOST 305-58 (sulfur content 1.0%); 13) the same; 14) D-11 + МК-22 + 3% ЦИАТИМ-339; 15) DS-11 + 6% ВНИИ НП-360; 16) the same + 6% ВНИИ НП-371; 17) the same + 8% МНИ ИП-22; 18) the same + 8.5% ПМС-19; 19) the same + 15% ИГ-102у.

diesels abroad is the attempt to use heavy residual fuels, i.e., residual fuel oil or mixtures of distillates and residual fuel oil including fuels with very high sulfur contents (up to 3-4%).

The utilization of heavy fuels is due primarily to their lower cost. Owing to the low cost and low consumption (in terms of weight) of fuel, high-power marine engines can compute successfully with steam-turbine installations.

The possibility of using heavy fuels in large slow-speed marine diesels has come about as a result of certain structural features of these engines and the utilization of special cylinder oils. In many engines of this type, the cylinder is separated from the crankcase by a diaphragm through which the piston rod passes, through a gland. This design prevents combustion products of the high-sulfur fuel and the cylinder oil from reaching the engine crankcase, and protects the crankcase oil against contamination.

The engine is lubricated separately; the oil used to lubricate the crankshaft-connecting rod mechanism is also used to cool the inside of the piston. The engine cylinders are lubricated by means of oil cups. Cylinder-oil consumption normally does not exceed 1.0 g/horsepower-hour.

Oil with a viscosity of 10-12 sst for 100°C is normally used to lubricate the crankshaft-connecting rod mechanism; it contains no additives or a small amount of antioxidant additive. When the engine is operated on heavy sulfur-bearing fuel, the cylinders are lubricated with more viscous oils containing more detergent antisulfur additive. In this country, we normally lubricate slow-speed diesels as follows: for the crankcase oil, a motor oil (GOST 1519-42) is used for the viscosity of 10-11 sst at 100°C, and for cylinder lubrication, AK-15 av-tol (GOST 1862-60) for the viscosity of 15 sst at 100°C, as well as

MS-20 oil (GOST 1013-49), while in many cases, the same motor oil is used for the cylinders. In an engine running on heavy sulfur-bearing fuels, however, these oils cannot reliably protect the engine against corrosion wear and the formation of deposits. In such case, it is necessary to use special cylinder oils.

In other countries [6], high-grade oils with viscosities of 15-25 sst at 100°C are used as cylinder oils; they contain alkali additives (for example, "Caltex," "Shell Tulsa Oil," "Gargoyle," etc.). They decrease sleeve wear when the engine uses a high-sulfur fuel.

The ESSO Company produces a special "TRO MAR DX-130" cylinder oil with a viscosity of 24 sst at 100°C; according to data supplied by the company, it decreases cylinder sleeve wear during operation of an engine with heavy sulfur-bearing fuels by 80% in comparison with a standard oil having no additives.

There is considerable interest in the so-called "emulsion oils," which have obtained limited application in marine engines.

Emulsion oils. Until recently, only substances that dissolve in petroleum products have been used as oil additives, i.e., organic com-

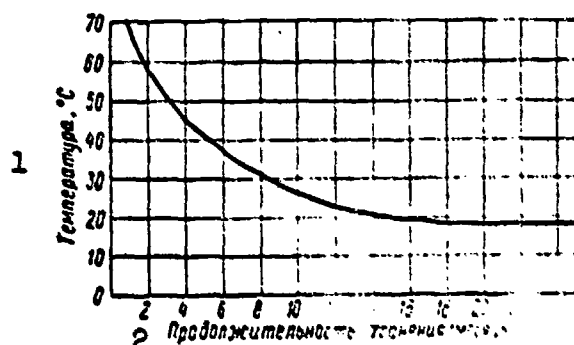


Fig. 35. Stability of Alexia emulsion oil as a function of temperature. 1) Temperature, °C; 2) storage time (months).

pounds, salts of organic acids such as naphthenates, sulfonates, as well as phenolates of various metals.

This has greatly limited the variety and decreased the effectiveness of

substances which could be used to improve the anticorrosion, antiwear, and other properties of lubricating oil, especially where engines are

operated on sulfur-bearing fuel.

The Shell Company has developed, tested, and marketed a new type

of so-called "emulsion" oil under the trade name Alexia-Shell; these oils contain a solution of additive distributed in the oil as an emulsion.

Alexia-Shell emulsion oil takes the form of an oily milky-white fluid, and it is designed only for engine cylinder lubrication by means of oil cups.

As analysis of imported Alexia-Shell emulsion oil has shown it is based on an ordinary base oil with viscosity of 16-18 sst at 100°C which contains, in the form of an emulsion, up to 30% of a water solution of calcium salts (in particular, calcium acetate).

Calcium acetate, which is the salt of a weak acid, has the properties of a base and, reacting with the sulfuric acid that forms on combustion of a sulfur-bearing fuel, neutralizes it, thus decreasing sleeve and piston-ring wear.

The most important requirement for this type of emulsion is stability, i.e., there should be no separation of the water phase from the oil with possible changes in ambient temperature.

The emulsion is stabilized by the introduction of special substances - stabilizers that prevent the colloidal system from coagulating, i.e., that prevent stratification of the emulsion oil.

Shell emulsion oil retains its stability at a temperature of 38°C for more than half a year. At higher temperatures, emulsion stability was less satisfactory. Figure 35 shows the stability of the emulsion oil as a function of temperature. As the temperature was lowered, the emulsion remained stable to -10°C. Here its viscosity increased, as with ordinary oils.

Tests of the emulsion oils used to lubricate cylinders of slow-speed diesel engines using heavy sulfur-bearing fuels have shown that the antiwear and anticarbon properties are better than those of ordi-

nary oils including oils with additives. A test carried out in a single-cylinder section of a two-cycle Sulzer engine using a heavy fuel having a viscosity at 50°C at 23° VU, a sulfur content of 3.5%, a carbon residue of 11% and an ash content of 0.08% has shown that the wear on the cylinder sleeve and piston rings decreased when emulsion oils were used to the level established when the engine was operated on diesel fuels and ordinary oils.

When emulsion oils replace ordinary oils, there is also a noticeable decrease in the carbon formed on exhaust ports and no carbon is found in the ring grooves. The amount of carbon in the combustion chamber was less, and it was lighter in color.

The results of bench tests carried out with sections of engines made it possible to organize broad-scale tests under operating conditions. These tests were arranged for an entire series of diesel-powered vessels equipped with two-cycle Burmeister and Wain, Doxford, Sulzer, MAN, Werkspur and other diesels.

Comparative data on wear was obtained by lubricating certain cylinders with emulsion oil while the remaining cylinders worked with standard oil.

Some of the results from these comprehensive tests are given in Table 38.

In all cases, the wear on cylinder sleeves lubricated with the emulsion oil was less than with the standard oil (by factors of 3 or 4, and even more in isolated cases).

The drawbacks inherent in emulsion oils include:

a) higher consumption of emulsion oil than regular oil, since the emulsion oil contains a considerable amount of water;

b) inadequate emulsion-oil stability at high temperatures. Thus, at 50°C, the oil cannot be stored for more than 3 months. Thus there



TABLE 33. Results of Operating Tests with Marine Diesels Using Standard and Emulsion Oils

1 Двигатель					2 Топливо			Средний расход топлива, 12 мм за 1000 час		15 Примечание		
3 Температура масла	4 Число цилиндров	5 Диаметр цилиндра, мм	6 Ход поршня, мм	7 Мощность, л. с.	8 Число оборотов, об/мин	9 Вязкость при 50°С, ВУ	10 Содержание серы, %	11 Коррозивность, %	13 на стандартном масле		14 на эмульсионном масле	
A	8	580	840	4000	245	13—20	3,0—3,5	10,0	0,50	0,14	16 Хромированные ступицы	17 Выходная часть ступицы
A	12	760	1250	12500	145	20—20,5	2,2—3,5	7,8	0,33	0,18		
B	12	680	1250	9600	125	40	3,5	12,5	0,70	0,10		
B	4	600	900	1800	165	45	1,1—3,2	12,0	0,15	0,06		
C	6	580	1250+450	7000	116	40	2,7—3,0	11,5	0,24	0,07	18 Прокрученная часть ступицы	
									0,32	0,12		

1) Engine; 2) fuel; 3) type of engine; 4) number of cylinders; 5) cylinder diameter, mm; 6) piston stroke, mm; 7) power, horsepower; 8) speed, rpm; 9) viscosity at 50°C, cSt; 10) sulfur content, %; 11) carbon residue, %; 12) mean cylinder-sleeve wear, mm per 1000 hours; 13) standard oil; 14) emulsion oil; 15) comments; 16) chromium-plated sleeves; 17) exhaust section of sleeve; 18) scavenging section of sleeve.

are certain difficulties involved in long-term storage and utilization of emulsion oils in tropical regions.

These emulsion-oil drawbacks have caused the Shell Company to market new grades of cylinder oils recently; they are based on naphthenates dissolved in the oil, and do not use water emulsions.

These oils are free the defects of emulsion oils, and at the same time have good antiwear and detergency properties.

In connection with the organization of production of large marine diesel engines in the Soviet Union, the question has arisen as to the creation of domestic cylinder oils that will make it possible to use heavy high-sulfur fuels with no decrease in engine motor potential. Preliminary tests of experimental specimens of special domestic cylinder oils have yielded satisfactory results.

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The numerator gives data on the top piston, and the denominator data on the bottom piston.

## CONCLUSION

Tests and operating experience with oils containing additives in various types of diesels have shown that the utilization of additives makes it possible to improve oil quality considerably and thus de-

TABLE 39. Proposed Diesel-Oil Classification

1.Группа	2 Тип масла	3 Назначение
В Б	4 Масла для обычных условий работы (серия 1)	7 Для смазки: а) малофорсированных дизелей; б) двигателей, работающих на топливах, с содержанием серы до 0,2%
У В	5 Масла для тяжелых условий работы (серия 2)	8 Для смазки: а) форсированных дизелей, работающих на топливах, с содержанием серы до 1,0%; б) дизелей, работающих на топливах, с содержанием серы более 1%
Г Г	6 Масла для особо тяжелых условий работы (серия 3)	9 Для смазки особо форсированных дизелей с высокой степенью наддува, работающих с переменной нагрузкой, на сернистом топливе

1) Group; 2) type of oil; 3) function; 4) oils for ordinary service conditions (series 1); 5) oils for heavy-duty service (series 2); 6) oils for especially severe service (series 3); 7) for lubricating: a) lightly supercharged diesels; b) engines using fuels containing up to 0.2% sulfur; 8) for lubricating: a) supercharged diesels using fuels containing up to 1.0% sulfur; b) diesels using fuels containing more than 1% sulfur; 9) for lubricating very highly supercharged diesels working with varying loads and running on high-sulfur fuels.

crease wear, reduce the amount of varnish and carbon deposits on engine parts, and improve operating conditions, i.e., in the last analysis, to increase engine reliability and service life.

At the same time, we should note that the quality and corresponding variety of oils used in diesel engines still does not correspond completely to operating requirements.

Diesel oils with TsiATIM-339 and AzNII-7 alkylphenol additives make it possible to operate low combustion-intensity diesels on fuels containing up to 1.0% sulfur.

Oils with phosphorus-containing VNII NP-360 additives are recommended for Type 2D100 supercharged diesels when fuels containing no more than 1.0% sulfur are used.

At the present time, we have no oils and additives for especially severe service conditions that can provide reliable operation of high combustion-intensity diesel engines using heavy gas-turbine supercharging when fuels with various sulfur contents are used. Only fuels with sulfur contents not exceeding 0.2% can be used to operate these diesel engines.

We also have no special cylinder oils to lubricate supercharged slow-speed marine diesels working on heavy fuels.

From the viewpoint of increasing service life (motor potential) of diesels of all types, regardless of combustion intensity, it is desirable to use oils with additives that possess better antiwear and detergency properties.

The existing motor-oil classification, which divides the variety of oils into automotive, tractor, diesel, aviation, and other classes does not correspond to the actual utilization of oils in engines.

It would be more desirable to classify oils on the basis of the severity of the conditions under which the oil must operate in the engine (allowing for the design and combustion intensity of the engine, operating conditions, fuel quality, etc.).

The basis for the diesel-oil classification should be the classification, given earlier (Chapter 1, Table 2) of diesel engines by degree of supercharging, which separates diesel engines into 3 groups on the basis of supercharging.

In accordance with this classification of diesel engines, and allowing for the utilization of fuels with various sulfur contents, the proposed oil classification will take the form shown in Table 39.

In addition to the three oil groups shown, it is also possible to have a temporary group A (series 0) oil classification, which will include oils not having additives or with relatively ineffective additives used to lubricate low combustion-intensity low-speed diesels of older design, and carburetor-type engines. As time passes, production of these oils will be curtailed, and they will be replaced by better-quality grades.

The oils of each group should be produced in the form of grades with varying viscosities ranging from 3 to 20 sst at 100°C such as, for example, M-10V, M-12V, M-16V, etc.

We still have no sufficiently reliable indices to characterize the quality of each type of oil. As a rough approximation, we may assume that the indices determined with laboratory apparatus should have the values for the oils in these groups shown in Table 40.

On the basis of the results of the tests discussed in Chapter 4, we may assume that the oils produced commercially containing the TsIA-TIM-339 and AzNII-7 alkylphenol additives will be classified as series 1 oils.

Oils with VNII NP-360 or MNI IP-22 additives may be classified arbitrarily as series 2 oils: for example, M-12V oil.

At the present time, we do not produce series 3 oils (for especially severe operating conditions).

Evaluation of oil quality on motorless apparatus, however, is at best preliminary in nature. The final classification of oils into the various groups should be carried out only on the basis of positive results from motor tests carried out in accordance with a special pro-

TABLE 40. Characteristics of Proposed Oils of Various Types as Evaluated on Laboratory Apparatus

1 Масло	Коррозийность по Пинкевичу, на свинцовой пластинке, 2 г/м <sup>2</sup> , не более	3 Окисляемость в приборе ДК-2 (осадок, %), не более	4 Моющие свойства по ПЗВ, баллы, не более	5 Термоокислительная стабильность по методу Папок, мин, не менее
6 Для обычных условий работы (серия 1) . . .	2,0	—	1,5	30
7 Для тяжелых условий работы (серия 2) . . .	1,0	5	0	50
8 Для особо тяжелых условий работы (серия 3)	0	0	0	70—80

1) Oil; 2) corrosiveness, Pinkevich method, lead plate, g/m<sup>2</sup>, no more than; 3) oxidizability in DK-2 apparatus (residue, %), no more than; 4) detergency, PZV method, arbitrary units, no more than; 5) thermal-oxidation stability, Papok method, min., no less than; 6) for ordinary operating conditions (series 1); 7) heavy-duty service (series 2); 8) especially severe service conditions (series 3).

gram on appropriate types of engines.

The new classification and associated suggestions as to improvement of the varieties of oils available will aid in increasing the quality of oils and additives for existing and future types of diesel engines.

Introduction of the new motor-oil classification and practical realization of the new catalogue of oils requires primarily:

a) the creation of new more effective oil additives that will make it possible to undertake production of types of oil presently in short supply, in particular, oils for especially severe service conditions (series 3);

b) the development of standard methods and special engines for performing motor tests on oils and additives that will be relevant to the various engine operating conditions.

This problem may be solved successfully by the combined efforts

of workers in the petroleum industry, diesel-engine plants, and consumers of petroleum products.

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